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## (54) RECORDING PAPER AND ITS MANUFACTURE

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a recording paper having high ink absorbing property, high glossiness, and high coating strength wherein dotted trouble is largely reduced.

SOLUTION: A recording paper comprises at least one recording layer having a void containing a hydrophilic binder and an inorganic fine particle arranged on a support, wherein the ratio of the inorganic fine particle to the hydrophilic binder in the recording layer is five times in weight ratio. As for the surface property at the recording layer side of the support, a maximum waviness is 4µm or less when a maximum filtered waviness is measured by making a reference length of a filtered wavy curve to be led under a condition of a cutoff value 0.8mm is set to 2.5mm from a measured sectional curve according to JIS-B-0610.

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# CLAIMS

## [Claim(s)]

[Claim 1] In the record form whose ratio of a non-subtlety particle [ as opposed to / have at least one layer of record layers which have an opening containing a hydrophilic binder and a non-subtlety particle on a base material, and / the hydrophilic binder of this record layer ] is 5 or more times in a weight ratio the filtering waviness curve to which the surface characteristic by the side of the record layer of this base material is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve measured according to JIS-B -0610 - as criteria die length of 2.5mm — filtering max, when a wave is measured The record form characterized by the maximum external waviness being 4 micrometers or less.

[Claim 2] The record form according to claim 1 characterized by the desiccation thickness of said record layer being 30 micrometers or more.

[Claim 3] The record form according to claim 1 or 2 characterized by the 75-degree specular gloss as which the glossiness of the front face of said record layer was specified to JIS-Z -8741 being 50% or more.

[Claim 4] A record form given in any 1 term of claims 1-3 to which said non-subtlety particle is characterized by being the particle silica compounded by the gaseous-phase method mean particle diameter has the primary [ an average of ] particle diameter which is 0.03-0.003 micrometers.

[Claim 5] A record form given in any 1 term of claims 1-4 characterized by said hydrophilic binder being polyvinyl alcohol or its derivative.

[Claim 6] A record form given in any 1 term of claims 1-5 characterized by containing the hardening agent over which said record layer can construct a bridge in a hydrophilic binder.

[Claim 7] A record form given in any 1 term of claims 1-6 characterized by being the paper base material with which said base material covered both sides of stencil paper with plastic resin.

[Claim 8] A record form given in any 1 term of claims 1-7 characterized by being the ink jet record form which a record form can record in water-soluble ink.

[Claim 9] It has at least one layer of record layers which have an opening containing a hydrophilic binder and a non-subtlety particle on a base material. The ratio of the non-subtlety particle to the hydrophilic binder of this record layer is 5 or more times in a weight ratio. the filtering waviness curve to which the surface characteristic by the side of the record layer of this base material is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve measured according to JIS-B -0610 — as criteria die length of 2.5mm — filtering max, when a wave is measured The manufacture approach of the record form characterized by drying once it cools after the maximum external waviness applies the coating liquid which forms this record layer in the manufacture approach of the record form which is 4 micrometers or less on said base material.

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#### **DETAILED DESCRIPTION**

# [Detailed Description of the Invention]

[0001]

[Field of the Invention] About the record form which records an image using color material, this invention has the reinforcement of high ink absorptivity and a highly-glossy and high coat especially in ink jet record, and, moreover, relates to few record form and its manufacture approach of a defect of a coat. [0002]

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple—color—izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0004] As a record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and generally it is required that the circumference should be smooth and should not fade etc.

[0005] As an ink jet record form, various record forms are used from the former. For example, a regular paper, various kinds of coated paper (art paper, coat paper, cast coated paper, etc.) which painted the layer which consists of a hydrophilic binder and an inorganic pigment on the paper base material, and the record form which painted the ink absorptivity layer as a record layer on various kinds of base materials which covered such papers, transparence, various kinds of opaque plastic film base materials, or both sides of paper with plastic resin further are used.

[0006] As the above-mentioned ink absorptivity layer, it is roughly divided into the so-called swelling type constituted by the subject in a hydrophilic binder of ink absorptivity layer, and the ink absorption layer of the opening mold which has an opening layer in a record layer.

[0007] Although the advantage of a swelling mold ink absorptivity layer is in the point that very high glossiness and high maximum density are obtained after an ink solvent (water and high-boiling point organic solvent) evaporates completely, since it is late compared with the opening mold record form which ink rate of absorption mentions later on the other hand, and there is a problem to which beading etc. is caused in a high ink field and the image quality by generating of ZARATSUKI tends to fall and evaporation of an ink solvent, especially a high-boiling point organic solvent is very slower still There is a problem accompanying being left on the damp or wet condition which the high-boiling point organic solvent remained and the hydrophilic binder swelled in the hydrophilic binder for a while after printing for a long period of time.

[0008] Specifically, it is in the situation that a printing front face cannot be strongly ground for several days by the case for several after [ printing ] hours, or paper etc. cannot be piled up.

[0009] On the other hand, since it has an opening in a record layer, the ink absorptivity layer of an opening mold shows high ink absorptivity. For this reason, in a high-density area, there is little degradation of image quality that beading of the image in a high ink field cannot happen easily as compared with a swelling mold.

[0010] Moreover, though the organic solvent remained in opening structure when the ink absorptivity layer of an opening mold had void volume of enough to the amount of ink, at least, a front face will be seemingly got dry immediately after printing, a front face is touched or it becomes once possible to pile up prints etc.

[0011] As this kind of an ink absorptivity layer, a particle with a particle size small moreover (especially 200nm or less is desirable) is preferably used from the point that a layer with comparatively high transparency is formed, with a low refractive index (about 1.6 or less refractive index is especially desirable), and it is especially used preferably from the silica particle which fulfills these conditions especially forming an opening efficiently, moreover comparatively high glossiness being acquired, and the image of high maximum density being obtained

etc.

[0012] As the conventional technique which uses a non-subtlety particle with such a small particle size for an ink jet record form, For example, JP,57–14091,A, 60–219083, 60–219084, JP,2–274857,A and 4–93284 — said — 5–51470 and 7–179029 — The colloidal silica indicated by each official report, such as 7–137431, 8–25800, 8–67064, and 8–118790, JP,3–56552,B, JP,63–170074,A, JP,2–113986,A, 2–187383, 7–276789, 8–34160, 8–132728 and the particle silica compounded by the gaseous-phase method indicated by each official report of No. 174992 [ eight to ], For example, JP,3–24906,B, 3–24907, 6–98844, 7–2430, said 121609 numbers, JP,60–245588,A, JP,2–43083,A, 2–198889, 2–263683, The porosity alumina indicated by 8–112964, 8–197832, 8–258397, etc. or its hydrate, For example, JP,57–120486,A, 57–129778, 58–55283, The particle calcium carbonate indicated by 61–20792, 63–57277, JP,4–250091,A, 3–251487, 4–250091, 4–260092, 7–40648, etc. is mentioned.

[0013] The record form which has the ink absorption layer of the above-mentioned opening mold on a base material is excellent in the point that high glossiness, high voidage, and high maximum density are obtained especially, and when the base material of moreover comparatively high smoothness is used, a record form with a high glossy surface is obtained.

[0014] And although voidage rises and it becomes easy to attain good ink absorptivity by smaller coverage so that the weight ratio of a non-subtlety particle to the hydrophilic binder of an opening layer is made to increase, the flexibility of a coat falls and it becomes easy to produce a very small crack in a spreading side in one side. When the ratio of a non-subtlety particle exceeds 5 times by the weight ratio especially to a hydrophilic binder, this problem tends to change notably.

[0015] Although this crack has improved greatly by adding a hydrophilic binder and the hardening agent which can construct a bridge, and the defects of a punctiform spreading side were few, there was a problem which still remains. As a result of examining many things about this cause, as for this problem, it turned out that the rigidity of an opening layer and the smoothness of a support surface are related.

[0016] That is, although the coat turned into a hard coat gradually in the process which a coat contracts at the time of the desiccation after spreading of an opening layer, since the rigidity of the coat at this time was too high, it turned out that it is for a minute crack to go into a coat locally with the very small wave and the irregularity of a support surface.

[0017] Even if the above-mentioned troubles are the case where the record layer which a coat becomes from a hydrophilic binder substantially is applied, and the case where a non-subtlety particle is used, they cannot become a not much big problem to less than 5% of the weight of a case easily to a hydrophilic binder.
[0018] It also became clear that it was much more easy to occur in the record form which is much more easy to generate the above-mentioned problem when it is easy to produce the local nonuniformity of the rate of drying of a spreading side in a desiccation process, and primary [ an average of ] particle size uses a particle 100nm or less as a subject, has high smoothness as a non-subtlety particle, and has the recording surface of high gloss.
[0019] A mean diameter uses [ specular gloss ] a non-subtlety particle and a hydrophilic binder 10nm or less for said JP,8-174992,A on 80% or more of polyolefine covering paper base material, and the ink jet record form which obtains high glossiness is indicated. However, the above-mentioned technical problem is not necessarily solved only by specifying the glossiness of a support surface.
[0020]

[Problem(s) to be Solved by the Invention] The technical problem which this invention is made in view of the above—mentioned actual condition, and this invention tends to solve is to offer the record form which improves the punctiform failure and the crack of a spreading side in the case of manufacture of the record form which has an opening layer as a record layer, and has high ink absorptivity, glossiness, and a film strength on a base material, and its manufacture approach.

[0021]

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the following configuration.

[0022] (1) In the record form whose ratio of a non-subtlety particle [ as opposed to / have at least one layer of record layers which have an opening containing a hydrophilic binder and a non-subtlety particle on a base material, and / the hydrophilic binder of this record layer ] is 5 or more times in a weight ratio the filtering waviness curve to which the surface characteristic by the side of the record layer of this base material is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve measured according to JIS-B -0610 - as criteria die length of 2.5mm — filtering max, when a wave is measured The record form characterized by the maximum external waviness being 4 micrometers or less.

[0023] (2) The record form of said one publication characterized by the desiccation thickness of said record layer being 30 micrometers or more.

[0024] (3) The record form of said 1 or 2 publications which are characterized by the 75-degree specular gloss as which the glossiness of the front face of said record layer was specified to JIS-Z -8741 being 50% or more. [0025] (4) A record form given in said any 1 term of 1-3 to which said non-subtlety particle is characterized by

being the particle silica compounded by the gaseous-phase method mean particle diameter has the primary [ an average of ] particle diameter which is 0.03-0.003 micrometers.

[0026] (5) A record form given in said any 1 term of 1-4 characterized by said hydrophilic binder being polyvinyl alcohol or its derivative.

[0027] (6) A record form given in said any 1 term of 1-5 characterized by containing the hardening agent over which said record layer can construct a bridge in a hydrophilic binder.

[0028] (7) A record form given in said any 1 term of 1-6 characterized by being the paper base material with which said base material covered both sides of stencil paper with plastic resin.

[0029] (8) A record form given in said any 1 term of 1-7 characterized by being the ink jet record form which a record form can record in water-soluble ink.

[0030] (9) It has at least one layer of record layers which have an opening containing a hydrophilic binder and a non-subtlety particle on a base material. The ratio of the non-subtlety particle to the hydrophilic binder of this record layer is 5 or more times in a weight ratio. the filtering waviness curve to which the surface characteristic by the side of the record layer of this base material is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve measured according to JIS-B -0610 — as criteria die length of 2.5mm — filtering max, when a wave is measured The manufacture approach of the record form characterized by drying once it cools after the maximum external waviness applies the coating liquid which forms this record layer in the manufacture approach of the record form which is 4 micrometers or less on said base material.

[0031] This invention is explained to a detail below. As a base material used for the record form of this invention, paper base materials, such as a regular paper, art paper, coat paper, and cast coated paper, the paper base materials which covered plastic film and both sides with polyolefine, or these compound base materials that were stuck are used.

[0032] As a plastic film base material, plastic film base materials, such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyethylenenaphthalate, triacetyl cellulose, a polyvinyl chloride, polyimide, a polycarbonate, and cellophane, etc. are desirable, for example.

[0033] These plastic film can use suitably a transparent thing, a translucent thing, and an opaque thing properly according to an application.

[0034] When considering as a white film, you may be the base material which prepared the layer which may use the base material which the plastic film base material was made to contain white pigments, such as a small amount of barium sulfate, titanium oxide, and a zinc oxide, and was obtained as it is, and has white pigments (titanium oxide, barium sulfate, etc.) in the side near the base material by the side of the rear face of a transparent film base material, or an ink absorptivity layer.

[0035] Moreover, the paper base material which covered both sides with the polyethylene usually conventionally used in color printing paper as a paper base material which covered both sides with polyolefine is desirable. In this case, it is desirable from making the titanium oxide of an anatase mold or a rutile mold contain seven to 15% of the weight to polyethylene not reducing the improvement in the opacity of a base material, or a whiteness degree, or the sharp nature of an image obtained into the polyethylene resin layer by the side of an ink absorptivity layer.

[0036] In this invention, when the paper base material which covered both sides with polyolefine especially is used, it is desirable from a viewpoint which controls generating of the punctiform defect of a spreading side, the effectiveness, i.e., the manufacture phase, of this invention.

[0037] Although it is carried out by spraying a wind on a spreading front face if needed in the process to dry, passing the field which is usually in an elevated-temperature condition about a spreading object after applying the coating liquid which forms a record layer on a base material in this case, for the evaporation heat of moisture, it usually comes out to become low, spreading skin temperature has it from ambient temperature, and supply of the heat energy for desiccation is mainly performed rather than a front face by heat transfer from the rear face of a base material to a record layer.

[0038] Since there is no porous layer and distribution of the heat energy resulting from partial unevenness, such as various kinds of rollers with which the rear face of a base material contacts, tends to appear in a spreading side as it is when a base material consists of plastic film, it becomes easy to go via uneven desiccation, and is easy to produce a punctiform defect as the result.

[0039] On the other hand, in the case of the paper base material with which the base material covered with polyolefin resin both sides which have a porous layer, since dispersion in heat tends to be eased by the longitudinal direction in paper, it is harder to produce such a defect.

[0040] the filtering waviness curve to which the base material used for the record form of this invention is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve by which the surface characteristic by the side of a record layer was measured according to JIS-B -0610 — as criteria die length of 2.5mm — filtering max — the time of measuring a wave — max — it is characterized by a wave being 4 micrometers or less.

[0041] Here, when a cross-section curve is cut at a right-angled flat surface on the surface of the recording

paper; it is the curve which appears in the cut end, and a filtering waviness curve is a curve which removes a surface roughness component with short wavelength from the above-mentioned cross-section curve using a low-pass filter, and is obtained. moreover, the wavelength corresponding to the frequency from which the gain becomes 70% when the low-pass filter of attenuation factor-12 dB/oct is used, in order that a cut-off value may ask for a filtering waviness curve — it is — max — a wave expresses the maximum wave height (WCM) in the criteria die length of the filtering maximum waviness curve per mum.

[0042] in addition — this invention — the above-mentioned max — a wave — ten places of arbitration — the max — a wave is measured and the value calculated as the average is used.

[0043] In this invention, the above-mentioned surface waviness was performed using the sensing-pin type surface roughness meter (surfboard COM 1500A, Tokyo Seimitsu Co., Ltd. make).

[0044] the above — setting — the smoothness of a base material — filtering max — expressing with a wave is not much for being hard to be influenced depending on the irregularity of shorter wavelength of the support surface which the method of expressing the smooth nature of a base material needs for acquiring the effectiveness of this invention.

[0045] It becomes large [ the effect to a punctiform defect ] more [ the direction of irregularity with more long wavelength ], so that the desiccation thickness of a record layer which has an opening is thick. If especially desiccation thickness exceeds 30 micrometers, most contribution of the minute irregularity of a support surface will be lost, and, generally contribution of a wave with more long wavelength will become remarkable.

[0046] Although the minimum of desiccation thickness is decided by the voidage and the amount of openings demanded of a coat, generally 15 micrometers or more are 20 micrometers or more preferably.

[0047] If the above WCM of the front face of a base material exceeds 4 micrometers, it will become easy to produce punctiform failure at the time of spreading desiccation of an opening layer. WCM is 3 micrometers or less preferably, and it is 2 micrometers or less especially preferably.

[0048] although the ink jet record form with which a mean diameter use a non-subtlety particle and a hydrophilic binder 10nm or less, and specular gloss obtain high glossiness on 80% or more of polyolefine covering paper base material be indicate by said JP,8-174992,A as a technique near the configuration of this invention, the flat surface property demand as high glossiness be not the irregularity with comparatively long wavelength like this invention but irregularity with short wavelength, and this applications differ clearly.

[0049] Moreover, the effect of the smoothness of a base material exerted on glossiness stops being influenced of the smoothness of a base material easily, and comes to depend for it on the glossiness of the opening layer itself chiefly so that the desiccation thickness of a record layer becomes large, but the description of being easy for the effect of a base material to come out is, so that the punctiform failure which is the effectiveness of this invention generally increases with increase of desiccation thickness and desiccation thickness increases.

[0050] it asks for the minute irregularity with the aforementioned short wavelength by measuring on conditions without being a measurement machine like the above and performing a high region cut-off — having (for example, approach indicated by JIS-B -0601) — all irregularity with short wavelength is also measured in this case.

[0051] Although the effectiveness of this invention can be acquired if the conditions of the above-mentioned external waviness are contained within the limits of this invention, when a component with the above-mentioned short wavelength is put in and measured, it is desirable that the maximum height per [ which is called for according to JIS-B -0601 ] criteria die length of 2.5mm is 6 micrometers or less, and especially 4 micrometers or less are the most desirable.

[0052] Next, especially the paper base material that covered both sides with the polyolefine used preferably is explained.

[0053] The stencil paper used for a paper base material uses wood pulp as the main raw material, and, in addition to wood pulp, paper making is carried out using synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, if needed. Although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used as wood pulp, it is desirable to use more many [ for a staple fiber ] LBKP, NBSP(s), LBSP(s), and NDP (s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0054] The pulp of the above-mentioned pulp which chemical pulp with few impurities (sulfate pulp and sulfite pulp) was used preferably, and performed bleaching processing, and raised the whiteness degree is also useful. [0055] Hara Kaminaka can add suitably flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc.

[0056] The freshness of the pulp used for paper making has desirable 200-500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of 24-mesh residue weight % and weight % of the 42-mesh residue as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it

is desirable that it is 20 or less % of the weight.

[0057] The basis weight of stencil paper has 60 thru/or desirable 250g, and 90 thru/or especially its 200g are desirable. The thickness of stencil paper has 50 thru/or desirable 250 micrometers.

[0058] After a paper-making phase or paper making, calender processing of the stencil paper can be carried out, and it can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m2 (JIS-P -8118). Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0059] A surface sizing compound may be applied to a stencil paper front face, and the sizing compound which can be added to said Hara Kaminaka as a surface sizing compound, and the same sizing compound can be used. [0060] When the hot water extraction method specified by JIS-P-8113 is resembled and it is measured more, pH of stencil paper can use a part of other LLDPE(s) (line low density polyethylene), polypropylene, etc., although polyethylene is desirable and is mainly the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density especially as polyolefine with which that it is 5-9 cover a desirable stencil paper front face and a desirable rear face.

[0061] As for especially the polyethylene layer by the side of an ink absorbing layer, what added the titanium oxide of a rutile or an anatase mold in polyethylene as widely performed by the printing paper for photographs, and improved opacity and a whiteness degree is desirable. A titanium oxide content is 5 – 15 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0062] After preparing an ink absorbing layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is damp and range whose 20-50-micrometer and back layer side the polyethylene layer by the side of an ink absorbing layer is 10-40 micrometers in general, although it is chosen so that the curl by highly-humid-izing may be optimized.

[0063] Furthermore, as for the above-mentioned polyethylene covering paper base material, it is desirable to have the following properties.

[0064] \*\* It is desirable that a lengthwise direction is [2 thru/or 30kg, and a longitudinal direction ] 1 thru/or 20kg by the reinforcement specified by :JIS-P -8113 in hauling strength.

[0065] \*\* 10 thru/or 300g, and a longitudinal direction have [ tear reinforcement / a lengthwise direction ] 20 thru/or desirable 400g by the convention approach by JIS-P -8116.

[0066] \*\* Clerks stiffness: 20-400g/100 are desirable.

[0067] \*\* Compressibility >=103 kgf/cm2\*\* surface smoothness: especially 1000 seconds or more have the desirable Beck smoothness specified to JIS-P -8119 500 seconds or more.

[0068] \*\* Surface glossiness: when it measures at the include angle of 75 degrees by the approach specified to JISZ-8741, it is 90% or more especially preferably 70% or more preferably 30% or more.

[0069] \*\* Surface whiteness degree: when it measures by the approach indicated by JIS-Z -8722 and displays according to JIS-Z -8729, [0070]

[External Character 1]

L\*は85%以上、特に90%以上が好ましい。また、 (a\*, b\*) は

(-2, 2)、(4, 2)、(4, -8) および(-3, -8) で囲ま

れる範囲の色鯛が好ましい。

[0071] \*\* Opacity: when it measures by the approach specified to JIS-P -8138, it is especially most preferably [ 94% or more of ] desirable 90% or more 50% or more.

[0072] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of a record layer for the purpose, such as to enlarge bond strength of the abovementioned base material and a record layer.

[0073] In this invention, it has at least one layer of opening layers which contain a hydrophilic binder and a non-subtlety particle on a base material as a record layer.

[0074] Although a non-subtlety particle with a small particle size is desirable at a low refractive index, for example, a silica, colloidal silica, a calcium silicate, a calcium carbonate, a boehmite aluminum hydroxide, or its hydrate is raised as the above-mentioned inorganic particle, it is a silica preferably.

[0075] A silica particle is divided roughly into dry process and a wet method according to a manufacturing method, and the approach by the gaseous—phase method hydrolysis in the elevated temperature of silicon halide and the approach of carrying out heating hydride generation of silica sand and the corks with an arc process with an electric furnace, and smothering this are learned as a dry—process particle silica. Moreover, after the acidolysis of silicate generates active silica as a wet method silica, carry out a polymerization moderately, and it is made to condense and precipitate, and is obtained.

[0076] The anhydrous silica compounded by the gaseous—phase method also in silica impalpable powder especially in this invention is desirable at the point that especially voidage and a strong film strength are obtained.

[0077] The mean particle diameter of the above-mentioned inorganic particle has a desirable thing 0.1 micrometers or less as the primary particle.

[0078] When a non-subtlety particle is a gaseous-phase method silica, the mean particle diameter of a primary particle is 0.003-0.03 micrometers, and 0.006-0.02 micrometers is especially the most desirable. Although the secondary gaseous-phase method silica is condensed in coating liquid and a bigger particle can be formed, the mean particle diameter of secondary floc has desirable 0.03-0.2 micrometers in this case.

[0079] In the above, the mean particle diameter of a non-subtlety particle observes the cross section and front face of the particle itself or an opening layer with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle size of the particle of 100 arbitration. The particle size of each [ here ] is expressed with the diameter when assuming a circle equal to the projected area. [0080] In the record form of this invention, as a hydrophilic binder used combining the above-mentioned inorganic particle, although polyvinyl alcohol and its derivative, polyalkylene oxide, a polyvinyl pyrrolidone, polyacrylamide, gelatin, hydroxyl ethyl cellulose, carboxyl methyl cellulose, a pullulan, casein, a dextran, etc. can be used, it is desirable from the point of the film strength immediately after printing that the bloating tendency and the solubility over the high-boiling point organic solvent and water which ink contains use a low hydrophilic binder.

[0081] In especially this invention, polyvinyl alcohol or its derivative is desirable, and average degree of polymerization is [ average degree of polymerization ] 2000 or more polyvinyl alcohol or a derivative of those most preferably 1000 or more especially. Moreover, whenever [ saponification / 70 - 100% of ] is desirable, and is especially the most desirable. [ 80 - 100% of ]

[0082] Although the above-mentioned hydrophilic binder can also be used together two or more sorts, even if it is this case, it is desirable to contain polyvinyl alcohol or its derivative at least 50% of the weight or more. [0083] As the above-mentioned poly BIRUARUKORU derivative, cation denaturation polyvinyl alcohol, anion denaturation polyvinyl alcohol, or Nonion denaturation polyvinyl alcohol is raised.

[0084] Cation denaturation polyvinyl alcohol is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0085] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-(- methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0086] the ratio of the cation denaturation radical content monomer of cation denaturation polyvinyl alcohol — vinyl acetate — receiving — 0.1–10-mol % — it is 0.2–5-mol % preferably.

[0087] the polymerization degree of cation denaturation polyvinyl alcohol — usually — 500-4000 — 1000-4000 are preferably desirable.

[0088] whenever [ moreover, / saponification / of a vinyl acetate radical ] — usually — 60-100 — it is 70-99 — mol % preferably.

[0089] The copolymer of the polyvinyl alcohol and JP,61–237681,A which have an anionic radical anion denaturation polyvinyl alcohol is indicated to be by JP,1–206088,A and vinyl alcohol which is indicated by the 63–307979 official report, and the vinyl compound which has a water–soluble radical, and the denaturation polyvinyl alcohol which has a water–soluble radical which is indicated by JP,7–285265,A are mentioned. [0090] Moreover, the polyvinyl alcohol derivative which added a polyalkylene oxide radical which is indicated by JP,7–9758,A to a part of vinyl alcohol as Nonion denaturation polyvinyl alcohol, for example, the block copolymer of the vinyl compound and vinyl alcohol which have the hydrophobic radical indicated by JP,8–25795,A, etc. are mentioned.

[0091] The ratio of the non-subtlety particle to the hydrophilic binder of the opening layer of the record form of this invention needs to be 5 or more times in a weight ratio, when obtaining high voidage and a high film strength. In being less than 5 times, the reinforcement of a coat tends to fall with the high-boiling point organic solvent as for which voidage falls and sufficient ink absorption capacity becomes is hard to be obtained and which remains in a hydrophilic binder after ink jet record. The ratio to the hydrophilic binder of a desirable non-subtlety particle is six or more.

[0092] The upper limit of the ratio of the non-subtlety particle to a hydrophilic binder is 20 or less in general from the crack engine performance of a coat.

[0093] It is desirable to add the hardening agent which can construct a bridge with said hydrophilic binder into the opening layer of the record form of this invention at the point of improving the film strength after printing which is amelioration of the film formation nature of an opening layer, the water resisting property of a coat, and the purpose of this invention. Inorganic hardening agents, such as an organic hardening agent which contains an epoxy group, an ethylene imino group, an activity vinyl group, etc. as such a hardening agent, chromium alum, a way acid, or way sand, are mentioned.

[0094] Especially when a hydrophilic binder is polyvinyl alcohol, the epoxy system hardening agent which has at least two epoxy groups in a molecule, a way acid or its salt, and way sand are desirable. As a way acid, not only an alt.way acid but a meta-way acid, a way [ degree ] acid, etc. can be used.

[0095] 1-200mg per above-mentioned binder [ hydrophilic ] 1g of additions of the above-mentioned hardening agent is 2-100mg preferably.

[0096] Various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of the ink jet record form of this invention.

[0097] For example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official report, The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of Nonion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, an acetic acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0098] Into the configuration layer of the arbitration by the side of the ink absorptivity of the record form of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,4-15744,B, JP,61-58788,A, and a 62-174184 official report, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0099] The amount of the spreading solid content by the side of the ink recording surface in the ink jet record form of this invention has in general desirable 5 - 40 g/m2, and its 10 - 30 g/m2 is more desirable.

[0100] When using the record form of this invention as a record form for ink jets, it is [ 1m of record forms ] desirable as void volume to be adjusted to the range preferably set to 15–30ml 10–40ml per two.

[0101] However, void volume is J.TAPPI. Paper pulp test method When the ink absorptivity side of a record form is measured by the approach indicated by the liquid absorptivity test method (Bristow law) of No.51 -87 paper and the paper board, absorption time amount is expressed with the amount of liquid transition in 2 seconds (ml/m2). In addition, although the liquid used at this time is pure water (ion exchange water), in order to make distinction of measurement area easy, less than 2% of water soluble dye may be contained.

[0102] The record form of this invention may have the record layer which has the above mentioned opening layer more than two-layer, and the ratios to the hydrophilic binder of the non-subtlety particle of the opening layer more than two-layer may differ in each other in this case.

[0103] Moreover, in addition to the above-mentioned opening layer, it may not have an opening layer but you may have the layer of bloating tendency to ink.

[0104] Such a swelling layer may be prepared in the upper layer (side which is separated from a base material) of the lower layer (side near a base material) of an opening layer, or an opening layer, and when there is an opening layer more than two-layer further, it may be prepared between opening layers. As an example of the hydrophilic binder which a hydrophilic binder is usually used for this bloating tendency layer, and is used here, the hydrophilic binder used for said opening layer is mentioned.

[0105] In order to adhere at the time of piling up immediately after curl prevention or printing to the opposite side and to raise a \*\* ink imprint further, as for the side which has the ink absorptivity layer of the record form of this invention, it is desirable to prepare the back layer of various classes.

[0106] Although the configuration of a back layer changes also with the class of base material, thickness, and the configuration and thickness of an ink absorptivity layer, generally a hydrophilic binder and a hydrophobic binder are used. The range of the thickness of a back layer is usually 0.1–10 micrometers.

[0107] Moreover, it adheres to a back layer as other record forms, and—izing of the front face can be carried out [ split face ] to prevention, note nature amelioration, and a pan for conveyance nature amelioration within an ink jet recording device. The organic or inorganic particle whose particle size is 2–20 micrometers is preferably used for this purpose.

[0108] Next, how to manufacture the record form of this invention is explained.

[0109] On a base material, the record form of this invention carries out spreading desiccation of the record layer which has an opening layer at least, and is obtained. The coating liquid (said additive added suitably a hydrophilic binder, a non-subtlety particle, and if needed is contained) which forms an opening layer is applied on a base material, and although it dries, if the temperature of coating liquid is dried after the thing of the range of 30–50 degrees C is usually used and it makes it once cool after applying on a base material, the punctiform failure at the time of desiccation will be mitigated in this case.

[0110] By once cooling coating liquid, the viscosity of coating liquid increases remarkably, the fluidity of a paint film falls and the nonuniformity of the paint film under the vibration at the time of conveyance or the effect of a wind decreases sharply. When there is nonuniformity of a paint film, punctiform failure in the part where

thickness increased not only increases, but partially, nonuniformity arises in void volume and there is [ whether it is a lifting and ] nothing to it about the serious effect for image quality.

[0111] From the temperature of coating liquid, the temperature of a paint film is preferably reduced by 20 degrees C or more, and evaporates 10 degrees C or more of a part of moisture and low-boiling point organic solvents in the condition. If this condition is reached, in order for the viscosity of a paint film to increase much more quickly and to approach a gelation condition, when it passes over this, even if it makes drying temperature increase, a paint film stops moving, and even if it dries a hot wind quickly [ delivery ], a good paint film side without nonuniformity or punctiform failure is acquired.

[0112] the once cooled temperature — the particle size of the non-subtlety particle of coating liquid, concentration, the class of hydrophilic binder and concentration, and the class of hardening agent and an amount — although it may change by various factors, such as an interaction of a non-subtlety particle and a hydrophilic binder, further, 0-20 degrees C is usually 5-15 degrees C preferably.

[0113] Although a cooldown delay may change by cooling temperature, humid thickness, etc., it is usually 10-60 seconds preferably for 5 to 200 seconds.

[0114] As for the desiccation after cooling, it is desirable to usually mention drying temperature gradually. Usually, finally it dries by 40–60–degree C warm air after fixed time amount desiccation at the temperature near a room temperature.

[0115] Because of the above-mentioned purpose, especially the viscosity property of coating liquid is important. It is coating liquid of 5 - 500cp extent at spreading temperature preferably, and at the time of cooling, 1000 or more cp is adjusted so that it may grow into a gelation condition preferably especially.

[0116] It is desirable to make it the viscosity ratio of coating liquid temperature and the temperature at the time of cooling become 100 or more times especially.

[0117] The approach of applying the above-mentioned opening layer on a base material can be suitably chosen from a well-known approach, and can be performed. As a spreading method, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain method of application, or given in a U.S. Pat. No. 2,681,294 official report is used preferably. [0118] Next, the record form of this invention is explained below about the water color ink in the case of using it as an ink jet record form.

[0119] Water color ink is usually water soluble dye and a solvent object, and a record liquid that consists of other additives. Although water soluble dye, such as direct dye well-known as water soluble dye at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0120] Although it becomes as a subject, when liquid ink dries water, in order that a color may deposit and the solvent of water color ink may prevent the blinding in a nozzle tip or an ink supply path, a high-boiling point organic solvent with the boiling point liquefied above about 120 degrees C is usually used at a room temperature. A high-boiling point organic solvent needs to have a high miscibility to water, while it is required that it should have vapor pressure far lower than water, since it has the operation which formed elements, such as a color, deposit and prevents generating of a big and rough sludge when water evaporates.

[0121] Although many organic solvents of a high-boiling point are usually used as a high-boiling point organic solvent for such the purpose As an example, ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the JICHIREN glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, Alcohols, such as 1, 2, 4-pentanetriol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, and a polyethylene glycol (average molecular weight is about 300 or less), are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0122] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, triethanolamine, and the triethylene glycol monobutyl ether etc. is desirable.

[0123] As an additive of others which water color ink contains, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rusr-proofer, etc. are mentioned, for example.

[0124] Water-color-ink liquid is the purpose which stabilizes the regurgitation from an ink jet nozzle in order to make wettability to a record form good, and in 25 degrees C, it is desirable to have the surface tension of 28 – 40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0125] Moreover, the viscosity of water color ink is usually 2.5 - 5cp preferably two to 8 cp in 25 degrees C.

[0126] The range of pH of water color ink is usually 4-10.

[0127] Since the diameter of the minimum dot with a diameter of about 20–60 micrometers is obtained in the record paper as a minimum liquid ink drop breathed out from an ink nozzle in the case of the capacity of 1–30x10–3nl, it is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. It is the case where the drop which has the volume of 2–20x10–3nl preferably is breathed out as the minimum drop.

[0128] Moreover, in the method recorded about a Magenta and cyanogen at least in the ink whose concentration is two kinds from which said water color ink differs more than twice respectively, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but this invention can be applied, also when this recording method is adopted.

[0129] In the ink jet record approach, as the record approach, various kinds of well-known methods can be used conventionally, and the detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0130] In the ink jet record approach of this invention, combining suitably approaches, such as making [ many / as possible ] thickness for the void volume of the record form which lessens the amount of maximum regurgitation ink as much as possible which lowers the ratio in the ink of a high-boiling point organic solvent, the approach of making void volume to the amount of high-boiling point organic solvents in the amount of the maximum ink 3 or more times sets up the optimal conditions, and is chosen.

[0131] As mentioned above, although the record form of this invention has been explained as a record form for ink jets the record form of this invention — except for ink jet record — a thermal—ink—transfer—printing method (the so—called melting mold hot printing method which is made to heat and carry out melting of the record ingredient containing the ink of thermofusion nature from an ink sheet base material side, and is made to record —) And it is applicable also to record forms, such as a record form for the so—called sublimation mold hot printing methods which heats like the record ingredient melting mold hot printing method which consists of a sublimation mold color and high softening—degree resin, and is recorded, and an electrophotography method. [0132]

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples.

[0133] The paper base material which covered both sides of 1160g of examples/, and the stencil paper for photographs of m2 with polyethylene (an anatase mold titanium dioxide is contained 13% of the weight in a polyethylene layer with a thickness [ by the side of a recording surface ] of 40 micrometers.) the back layer which the thickness of the polyethylene layer by the side of a rear face makes solid content the Tg=65 degree C diameter latex resin of an acrylic on a polyethylene layer by 25 micrometers, and is contained two times 0.3 g/m by making into a mat agent the silica 0.6g/m2, and whose mean diameter are about 13 micrometers — having — it prepared.

[0134] As a property of the above-mentioned polyethylene covering paper, it asked for glossiness, WCM, and the maximum height (the criteria die length found according to JIS-0601 is the maximum height per 2.5mm, and mum unit), and was shown in Table 1.

[0135] Next, 150g of primary particle silica powder whose mean particle diameter is about 7nm was added in 1000ml of pure water, the high-speed homogenizer distributed, and pale clear dispersion liquid were obtained. Next, in this silica water dispersion (I), average degree of polymerization added gradually 2% polyvinyl alcohol water-solution (II) (ethyl acetate is contained 6% of the weight)1000ml whenever [ saponification / whose ] is 88% by 3500. Subsequently, 40ml of 4% way sand water solutions was added as a hardening agent, the high-speed homogenizer distributed, and white translucent-like coating liquid was obtained. This liquid contains the silica 7.5 times by the weight ratio to polyvinyl alcohol. Moreover, the viscosity of the above-mentioned coating liquid was 50,000cp when it measured by the Brookfield viscometer, and it measured at 60cp and 15 degrees C by 40 degrees C.

[0136] Subsequently, the 40-degree C coating liquid obtained as mentioned above was applied to the recording surface side of the above-mentioned polyethylene covering paper, and was made to once cool so that spreading coat temperature may turn to 15 degrees C or less (for 20 seconds). Subsequently, the 25-degree C wind was sprayed for the 20-degree C wind for 30 seconds, for 60 seconds and a 45 more-degree C wind were sprayed for 30 seconds and for a 35-degree C wind one by one for 120 seconds, it dried, 25 more degrees C and the ambient atmosphere of 50% of relative humidity were passed for 30 seconds, gas conditioning was carried out, and the record form -1 was produced.

[0137] Next, record form which covered the same polyethylene layer as the record form -1 on the front reverse side in the record form -1 using the various stencil paper with which smooth nature differs as stencil paper of a base material - 2-4 were produced like the record form -1. Record form - The optical property and smooth nature after polyethylene covering of 1-4 were shown in Table 1.

[0138] Record form - 1-4 were saved for three days at 39 degrees C by the condition of having wound in the shape of a roll, after spreading desiccation.

[0139] It evaluated about the following items [ form / which was obtained / record ].

[0140] (1) Void volume Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used, and the amount of transition for [ contact time ] 2 seconds (ml/m2) was calculated as void volume. [0141] (2) Contact time calculated ink absorptivity from the amount of transition in 0.5 seconds (ml/m2) using the same testing machine as having measured ink absorptivity void volume.

[0142] (3) The specular gloss was measured 75 degrees with the deflection photometer (VGS-101DP) by glossiness Nippon Denshoku Industries Co., Ltd.

[0143] (4) The surface punctiform defective number was investigated about the spreading sample of 10x10cm of failure defects.

[0144] (5) After 23 degrees C and relative humidity saved at 80% after solid printing for 24 hours by the ink jet printer by film strength Seiko Epson, Inc., and MJ-5100C, it scratched in the same environment, the tip applied the continuation load (0-100g) to the sapphire needle of 0.3mmphi using the strength test machine (Hayden try BOGIA, new east science incorporated company make), the film strength was examined, and reinforcement by which a coat is destroyed was made into the film strength.

[0145] If it is 30g or more in general by this evaluation approach, it can be said that it has the practically sufficiently high film strength.

[0146] In addition, in (1) and (2), the used ink used the ink which contains a water-soluble Magenta color for a diethylene glycol 1% of the weight 20% of the weight. A result is shown in Table 1.
[0147]

# [Table 1]

記録用紙	支	持体の特	性	記録層無機微粒子/		記録用紙の特性					
	光沢度	Wem	ち高大最	親水性バッチー	乾燥膜厚	空隙容量	心吸収性	光沢度	故障欠陥	皮膜強度	
記録用紙-1(本発明) 記録用紙-2(本発明) 記錄用紙-3(本発明) 記録用紙-4(比較例)	93% : 91% :	1. 2 µm 2. 3 µm 3. 5 µm 5. 2 µm	1.9μm 4.1μm 5.2μm 6.3μm	7.5 7.5 7.5 7.5	38 µm 38 µm 38 µm 38 µm	24ml 24ml 24ml 24ml	16m i 16m i 16m i	61% 61% 61% 53%	0 1 12 >100	72 g 69 g 70 g 73 g	

[0148] Record form whose WCM is 4 micrometers or less when changing the class of stencil paper and changing the surface characteristic after covering from the result of Table 1 with polyethylene resin – 1–3 are understood that there are few failure defects compared with the record form –4 with which WCM exceeds 4 micrometers. [0149] When especially WCM uses the base material which is 2 micrometers or less, a failure defect is desirable at 0.

[0150] Moreover, according to the difference of a base material, void volume and ink absorptivity are hardly influenced, but desiccation thickness is 30 micrometers or more, and since it has high voidage (about 63%), void volume almost sufficient by the usual ink jet record is held.

[0151] The coating liquid which forms the opening layer which prepared the polyethylene covering paper base material to which the thickness of the polyethylene layer by the side of a recording surface was changed in the record form -1 produced in the example 2 example 1 as shown in Table 2, and was produced in the example 1 is applied like an example 1, and it is a record form. - 21-24 were produced. Record form with which various clearing-up processings are performed for a front face immediately after painting the polyethylene layer on a side front in the Hara paper, and surface characteristics differ on the other hand in the record form -1 produced in the example 1 - 25-27 were produced like the record form -1.

[0152] The die length of a pitch in which the base material of the record form -25 is called the so-called silky surface is clearing up of hundreds of micrometer unit, and that of the base material of the record form -27 is the detailed mat side where clearing up is called the so-called mat side. The record forms -26 are these middle. [0153] Furthermore, the base material of the record form -28 processes and split-face-izes the support surface of the record form -1 with a 40-degree C acetone solution. Usually, effectiveness is in the increase of an adhesive property [ be / they / these split faces ] of a base material and a record layer.

[0154] Record form – The property after applying the surface characteristic and record layer of polyethylene covering paper of 21–28 was evaluated like the example 1. A result is shown in Table 2. [0155] [Table 2]

記録用紙	ポリエチレ	ン層		支持体の特	记錄層	記録用紙の特性			
nto ≥ 711 der	厚み (μm)	片付け	光沢度	Wc∎	最大高さ	無機微粒子/	光沢度	故障欠陥	皮膜強度
記録用紙-21(本発明)	30 µ m	無	92%	1.7µm	2.1 µ m	7.5	59%	0	71 g
記錄用紙-22(本発明)	20 µ m	無	85%	2.5µm	3.4 µ m	7.5	58%	2	70 g
記録用紙-23(本発明)	15 µ m	無	71%	3. 2 $\mu$ m	5. 2 µ m	7.5	58%	10	73 g
記録用柢-24(比較例)	10 µ m	無	56%	4.7µm	7.1µm	7. 5	51%	90	68 g
記録用紙-25(比較例)	40 µ m	有	46%	5.8µm	7.8µm	7. 5	50%	>100	44 g
記錄用紙-26(比較例)	40 $\mu$ m	有	9%	4.6 µ m	6.3 µ m	7. 5	36%	>100	68 g
記録用紙-27(本発明)	40 µ m	有	5%	3.3 µ m	3.2 µ m	7. 5	41%	. 8	67 g
記錄用紙-28(本発明)	40 µ m	粗面化	18%	2.3 µ m	3.1 µ m	7.5	53%	3	68 g

[0156] Record form of this invention the result of Table 2 to whose WCM is 4 micrometers or less – 21, 22, and 23 are understood that there are few failure defects as compared with the comparative record form –24. Moreover, it turns out that WCM is excellent in the record form –21 2 micrometers or less especially especially like an example 1.

[0157] Record form whose WCM is 4 micrometers or less even if it is the case where tidied up and processed the front face of a polyethylene resin layer, or split-face-ized on the other hand, and the glossiness of a base material uses a low thing – 27 and 28 are understood that there are few failure defects. Moreover, when WCM exceeds 4 micrometers also in a clearing-up base material, it turns out that a failure defect increases quickly. [0158] Record form which has desiccation thickness as humid thickness is changed and shows the coating liquid produced in the example 1 on the polyethylene covering paper base material for record form-4 produced in the example of comparison 1 example 1 in Table 3 – 31–34 were produced like the record form –4.

[0159] The result which estimates as an example 1 similarly and is shown in Table 3 was obtained. [0160]

[Table 3]

記録用紙	支持体の特性	記 録 層 無機磁粒子/		記録用紙の特性						
	W <sub>CM</sub> 親水性パンダー	乾燥膜厚	<b>室</b> 客網空	インク吸収性	光沢度	故障欠陷				
記録用紙-31(比較例) 記録用紙-32(比較例) 記錄用紙-33(比較例) 記錄用紙-34(比較例)	5.2µm 5.2µm 5.2µm 5.2µm	7.5 7.5 7.5 7.5	45 μ m 30 μ m 25 μ m 20 μ m	29m! 19mi 16mi 12mi	21 m l 1 î m l 7 m l 4 m l	52% 51% 62% 64%	>100 >100 58 20			

[0161] Since void volume falls gradually in connection with this although a failure defect will fall if desiccation thickness is decreased even if WCM uses the base material exceeding 4 micrometers from the result of Table 3, it is a record form. – 31–34 cannot be used practical.

[0162] Record form produced in the example 3 example 1 – It is a record form except having changed the particle silica into the gaseous-phase method [ the mean particle diameter of a primary particle is about 20nm ] silica in 1-4. – It is a record form like 1-4. – 41-44 were produced. It was similarly estimated as the example 1 and the result shown in Table 4 was obtained.

[Table 4]

記録用紙	支持体の特性	記 錄 唐 無機微粒子/	記録用紙の特性							
	Wcm	親水性パインダー	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度		
記録用紙-41(本発明) 記錄用紙-42(本発明) 記録用紙-43(本発明) 記録用紙-44(比較例)	1. 2 µ m 2. 3 µ m 3. 5 µ m 5. 2 µ m	7. 5 7. 5 7. 5 7. 5	38 µ m 38 µ m 38 µ m 38 µ m	26m l 26m l 26m l 26m l	19ml 19ml 19ml 19ml	54% 52% 51% 51%	0 3 15 >100	60 g 57 g 58 g 53 g		

[0164] The result of Table 4 shows that the same effectiveness as an example 1 is acquired. However, the glossiness of a recording surface falls with increase of the particle size of the primary particle of a silica more slightly than an example 1, and void volume is increasing a little.

[0165] 150g of primary particle silica powder whose example of comparison 2 mean particle diameter is about 7nm was added in 1000ml of pure water, the high-speed homogenizer distributed, and pale clear dispersion liquid were obtained. Next, in this silica water dispersion (I), average degree of polymerization added gradually 2% polyvinyl alcohol water-solution (II) (ethyl acetate is contained 6% of the weight)2000ml whenever [ saponification / whose ] is 88% by 3500. Subsequently, 40ml of 4% way sand water solutions was added as a hardening agent, the high-speed homogenizer distributed, and white translucent-like coating liquid was obtained. This liquid contains the silica 3.75 times by the weight ratio to polyvinyl alcohol.

[0166] Record form used in the example 1 – With the polyethylene of 1–4, it applies in the covering paper so that desiccation thickness may become being the same as that of an example 1 about the above-mentioned coating liquid, and humid thickness may be set to 170 micrometers, and it dries by the approach indicated by the example 1, and is a record form. – 51–54 were produced. It was similarly estimated as the example 1 and the result shown in Table 5 was obtained.

## [0167]

# [Table 5]

記録用紙	支持体の特性	記録 層無機微粒子/	記録用紙の特性							
,	Wcm	親水性パンダー	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度		
記録用紙-51(比較明) 記録用紙-52(比較明) 記録用紙-53(比較明) 記録用紙-54(比較例)	1. 2 µm 2. 3 µm 3. 5 µm 5. 2 µm	3. 75 3. 75 3. 75 3. 75	38 µ m 38 µ m 38 µ m 38 µ m	15ml 15ml 15ml 15ml	4m l 4m l 4m l 4m l	81% 80% 80% 78%	0 0 0 3	17g 15g 15g 14g		

[0168] Although a failure defect is hardly produced from the result shown in Table 5 even if WCM uses the thing exceeding 4 micrometers as a base material when the ratio to the hydrophilic binder of a non-subtlety particle is made or less into five, but the glossiness of a recording surface is also very high, it turns out that void volume falls and the reinforcement of a coat falls greatly.

[0169]

[Effect of the Invention] As mentioned above, if this invention is followed, it will have high ink absorptivity, high-glossiness, and high paint film reinforcement, and the record form which moreover decreased punctiform failure greatly will be obtained.

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## **TECHNICAL FIELD**

[Field of the Invention] About the record form which records an image using color material, this invention has the reinforcement of high ink absorptivity and a highly-glossy and high coat especially in ink jet record, and, moreover, relates to few record form and its manufacture approach of a defect of a coat.

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#### **PRIOR ART**

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0004] As a record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and generally it is required that the circumference should be smooth and should not fade etc.

[0005] As an ink jet record form, various record forms are used from the former. For example, a regular paper, various kinds of coated paper (art paper, coat paper, cast coated paper, etc.) which painted the layer which consists of a hydrophilic binder and an inorganic pigment on the paper base material, and the record form which painted the ink absorptivity layer as a record layer on various kinds of base materials which covered such papers, transparence, various kinds of opaque plastic film base materials, or both sides of paper with plastic resin further are used.

[0006] As the above-mentioned ink absorptivity layer, it is roughly divided into the so-called swelling type constituted by the subject in a hydrophilic binder of ink absorptivity layer, and the ink absorption layer of the opening mold which has an opening layer in a record layer.

[0007] Although the advantage of a swelling mold ink absorptivity layer is in the point that very high glossiness and high maximum density are obtained after an ink solvent (water and high-boiling point organic solvent) evaporates completely, since it is late compared with the opening mold record form which ink rate of absorption mentions later on the other hand, and there is a problem to which beading etc. is caused in a high ink field and the image quality by generating of ZARATSUKI tends to fall and evaporation of an ink solvent, especially a high-boiling point organic solvent is very slower still There is a problem accompanying being left on the damp or wet condition which the high-boiling point organic solvent remained and the hydrophilic binder swelled in the hydrophilic binder for a while after printing for a long period of time.

[0008] Specifically, it is in the situation that a printing front face cannot be strongly ground for several days by the case for several after [ printing ] hours, or paper etc. cannot be piled up.

[0009] On the other hand, since it has an opening in a record layer, the ink absorptivity layer of an opening mold shows high ink absorptivity. For this reason, in a high-density area, there is little degradation of image quality that beading of the image in a high ink field cannot happen easily as compared with a swelling mold.

[0010] Moreover, though the organic solvent remained in opening structure when the ink absorptivity layer of an opening mold had void volume of enough to the amount of ink, at least, a front face will be seemingly got dry immediately after printing, a front face is touched or it becomes once possible to pile up prints etc.

[0011] As this kind of an ink absorptivity layer, a particle with a particle size small moreover (especially 200nm or less is desirable) is preferably used from the point that a layer with comparatively high transparency is formed, with a low refractive index (about 1.6 or less refractive index is especially desirable), and it is especially used preferably from the silica particle which fulfills these conditions especially forming an opening efficiently, moreover comparatively high glossiness being acquired, and the image of high maximum density being obtained etc.

[0012] As the conventional technique which uses a non-subtlety particle with such a small particle size for an ink jet record form, For example, JP,57-14091,A, 60-219083, 60-219084, JP,2-274857,A and 4-93284 — said — 5-51470 and 7-179029 — The colloidal silica indicated by each official report, such as 7-137431, 8-25800, 8-67064, and 8-118790, JP,3-56552,B, JP,63-170074,A, JP,2-113986,A, 2-187383, 7-276789, 8-34160, 8-132728 and the particle silica compounded by the gaseous-phase method indicated by each official report of No. 174992

[ eight to ], For example, JP,3-24906,B, 3-24907, 6-98844, 7-2430, said 121609 numbers, JP,60-245588,A, JP,2-43083,A, 2-198889, 2-263683, The porosity alumina indicated by 8-112964, 8-197832, 8-258397, etc. or its hydrate, For example, JP,57-120486,A, 57-129778, 58-55283, The particle calcium carbonate indicated by 61-20792, 63-57277, JP,4-250091,A, 3-251487, 4-250091, 4-260092, 7-40648, etc. is mentioned.

[0013] The record form which has the ink absorption layer of the above-mentioned opening mold on a base material is excellent in the point that high glossiness, high voidage, and high maximum density are obtained especially, and when the base material of moreover comparatively high smoothness is used, a record form with a high glossy surface is obtained.

[0014] And although voidage rises and it becomes easy to attain good ink absorptivity by smaller coverage so that the weight ratio of a non-subtlety particle to the hydrophilic binder of an opening layer is made to increase, the flexibility of a coat falls and it becomes easy to produce a very small crack in a spreading side in one side. When the ratio of a non-subtlety particle exceeds 5 times by the weight ratio especially to a hydrophilic binder, this problem tends to change notably.

[0015] Although this crack has improved greatly by adding a hydrophilic binder and the hardening agent which can construct a bridge, and the defects of a punctiform spreading side were few, there was a problem which still remains. As a result of examining many things about this cause, as for this problem, it turned out that the rigidity of an opening layer and the smoothness of a support surface are related.

[0016] That is, although the coat turned into a hard coat gradually in the process which a coat contracts at the time of the desiccation after spreading of an opening layer, since the rigidity of the coat at this time was too high, it turned out that it is for a minute crack to go into a coat locally with the very small wave and the irregularity of a support surface.

[0017] Even if the above-mentioned troubles are the case where the record layer which a coat becomes from a hydrophilic binder substantially is applied, and the case where a non-subtlety particle is used, they cannot become a not much big problem to less than 5% of the weight of a case easily to a hydrophilic binder.
[0018] It also became clear that it was much more easy to occur in the record form which is much more easy to generate the above-mentioned problem when it is easy to produce the local nonuniformity of the rate of drying of a spreading side in a desiccation process, and primary [ an average of ] particle size uses a particle 100nm or less as a subject, has high smoothness as a non-subtlety particle, and has the recording surface of high gloss.
[0019] A mean diameter uses [ specular gloss ] a non-subtlety particle and a hydrophilic binder 10nm or less for said JP,8-174992,A on 80% or more of polyolefine covering paper base material, and the ink jet record form which obtains high glossiness is indicated. However, the above-mentioned technical problem is not necessarily solved only by specifying the glossiness of a support surface.

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### **EFFECT OF THE INVENTION**

[Effect of the Invention] As mentioned above, if this invention is followed, it will have high ink absorptivity, high-glossiness, and high paint film reinforcement, and the record form which moreover decreased punctiform failure greatly will be obtained.

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#### TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The technical problem which this invention is made in view of the above-mentioned actual condition, and this invention tends to solve is to offer the record form which improves the punctiform failure and the crack of a spreading side in the case of manufacture of the record form which has an opening layer as a record layer, and has high ink absorptivity, glossiness, and a film strength on a base material, and its manufacture approach.

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#### **MEANS**

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the following configuration.

[0022] (1) In the record form whose ratio of a non-subtlety particle [ as opposed to / have at least one layer of record layers which have an opening containing a hydrophilic binder and a non-subtlety particle on a base material, and / the hydrophilic binder of this record layer ] is 5 or more times in a weight ratio the filtering waviness curve to which the surface characteristic by the side of the record layer of this base material is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve measured according to JIS-B -0610 - as criteria die length of 2.5mm — filtering max, when a wave is measured The record form characterized by the maximum external waviness being 4 micrometers or less.

[0023] (2) The record form of said one publication characterized by the desiccation thickness of said record layer being 30 micrometers or more.

[0024] (3) The record form of said 1 or 2 publications which are characterized by the 75-degree specular gloss as which the glossiness of the front face of said record layer was specified to JIS-Z -8741 being 50% or more. [0025] (4) A record form given in said any 1 term of 1-3 to which said non-subtlety particle is characterized by being the particle silica compounded by the gaseous-phase method mean particle diameter has the primary [ an average of ] particle diameter which is 0.03-0.003 micrometers.

[0026] (5) A record form given in said any 1 term of 1-4 characterized by said hydrophilic binder being polyvinyl alcohol or its derivative.

[0027] (6) A record form given in said any 1 term of 1-5 characterized by containing the hardening agent over which said record layer can construct a bridge in a hydrophilic binder.

[0028] (7) A record form given in said any 1 term of 1–6 characterized by being the paper base material with which said base material covered both sides of stencil paper with plastic resin.

[0029] (8) A record form given in said any 1 term of 1-7 characterized by being the ink jet record form which a record form can record in water-soluble ink.

[0030] (9) It has at least one layer of record layers which have an opening containing a hydrophilic binder and a non-subtlety particle on a base material. The ratio of the non-subtlety particle to the hydrophilic binder of this record layer is 5 or more times in a weight ratio. the filtering waviness curve to which the surface characteristic by the side of the record layer of this base material is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve measured according to JIS-B -0610 — as criteria die length of 2.5mm — filtering max, when a wave is measured The manufacture approach of the record form characterized by drying once it cools after the maximum external waviness applies the coating liquid which forms this record layer in the manufacture approach of the record form which is 4 micrometers or less on said base material.

[0031] This invention is explained to a detail below. As a base material used for the record form of this invention, paper base materials, such as a regular paper, art paper, coat paper, and cast coated paper, the paper base materials which covered plastic film and both sides with polyolefine, or these compound base materials that were stuck are used.

[0032] As a plastic film base material, plastic film base materials, such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyethylenenaphthalate, triacetyl cellulose, a polyvinyl chloride, polyimide, a polycarbonate, and cellophane, etc. are desirable, for example.

[0033] These plastic film can use suitably a transparent thing, a translucent thing, and an opaque thing properly according to an application.

[0034] When considering as a white film, you may be the base material which prepared the layer which may use the base material which the plastic film base material was made to contain white pigments, such as a small amount of barium sulfate, titanium oxide, and a zinc oxide, and was obtained as it is, and has white pigments (titanium oxide, barium sulfate, etc.) in the side near the base material by the side of the rear face of a transparent film base material, or an ink absorptivity layer.

[0035] Moreover, the paper base material which covered both sides with the polyethylene usually conventionally used in color printing paper as a paper base material which covered both sides with polyolefine is desirable. In

this case, it is desirable from making the titanium oxide of an anatase mold or a rutile mold contain seven to 15% of the weight to polyethylene not reducing the improvement in the opacity of a base material, or a whiteness degree, or the sharp nature of an image obtained into the polyethylene resin layer by the side of an ink absorptivity layer.

[0036] In this invention, when the paper base material which covered both sides with polyolefine especially is used, it is desirable from a viewpoint which controls generating of the punctiform defect of a spreading side, the effectiveness, i.e., the manufacture phase, of this invention.

[0037] Although it is carried out by spraying a wind on a spreading front face if needed in the process to dry, passing the field which is usually in an elevated-temperature condition about a spreading object after applying the coating liquid which forms a record layer on a base material in this case, for the evaporation heat of moisture, it usually comes out to become low, spreading skin temperature has it from ambient temperature, and supply of the heat energy for desiccation is mainly performed rather than a front face by heat transfer from the rear face of a base material to a record layer.

[0038] Since there is no porous layer and distribution of the heat energy resulting from partial unevenness, such as various kinds of rollers with which the rear face of a base material contacts, tends to appear in a spreading side as it is when a base material consists of plastic film, it becomes easy to go via uneven desiccation, and is easy to produce a punctiform defect as the result.

[0039] On the other hand, in the case of the paper base material with which the base material covered with polyolefin resin both sides which have a porous layer, since dispersion in heat tends to be eased by the longitudinal direction in paper, it is harder to produce such a defect.

[0040] the filtering waviness curve to which the base material used for the record form of this invention is led on with a cut-off value [ of 0.8mm ] conditions from the cross-section curve by which the surface characteristic by the side of a record layer was measured according to JIS-B -0610 — as criteria die length of 2.5mm — filtering max — the time of measuring a wave — max — it is characterized by a wave being 4 micrometers or less. [0041] Here, when a cross-section curve is cut at a right-angled flat surface on the surface of the recording paper, it is the curve which appears in the cut end, and a filtering waviness curve is a curve which removes a surface roughness component with short wavelength from the above-mentioned cross-section curve using a low-pass filter, and is obtained, moreover, the wavelength corresponding to the frequency from which the gain becomes 70% when the low-pass filter of attenuation factor-12 dB/oct is used, in order that a cut-off value may ask for a filtering waviness curve — it is — max — a wave expresses the maximum wave height (WCM) in the criteria die length of the filtering maximum waviness curve per mum.

[0042] in addition — this invention — the above-mentioned max — a wave — ten places of arbitration — the max — a wave is measured and the value calculated as the average is used.

[0043] In this invention, the above-mentioned surface waviness was performed using the sensing-pin type surface roughness meter (surfboard COM 1500A, Tokyo Seimitsu Co., Ltd. make).

[0044] the above — setting — the smoothness of a base material — filtering max — expressing with a wave is not much for being hard to be influenced depending on the irregularity of shorter wavelength of the support surface which the method of expressing the smooth nature of a base material needs for acquiring the effectiveness of this invention.

[0045] It becomes large [ the effect to a punctiform defect ] more [ the direction of irregularity with more long wavelength ], so that the desiccation thickness of a record layer which has an opening is thick. If especially desiccation thickness exceeds 30 micrometers, most contribution of the minute irregularity of a support surface will be lost, and, generally contribution of a wave with more long wavelength will become remarkable.

[0046] Although the minimum of desiccation thickness is decided by the voidage and the amount of openings demanded of a coat, generally 15 micrometers or more are 20 micrometers or more preferably.

[0047] If the above WCM of the front face of a base material exceeds 4 micrometers, it will become easy to produce punctiform failure at the time of spreading desiccation of an opening layer. WCM is 3 micrometers or less preferably, and it is 2 micrometers or less especially preferably.

[0048] although the ink jet record form with which a mean diameter use a non-subtlety particle and a hydrophilic binder 10nm or less, and specular gloss obtain high glossiness on 80% or more of polyolefine covering paper base material be indicate by said JP,8-174992,A as a technique near the configuration of this invention, the flat surface property demand as high glossiness be not the irregularity with comparatively long wavelength like this invention but irregularity with short wavelength, and this applications differ clearly.

[0049] Moreover, the effect of the smoothness of a base material exerted on glossiness stops being influenced of the smoothness of a base material easily, and comes to depend for it on the glossiness of the opening layer itself chiefly so that the desiccation thickness of a record layer becomes large, but the description of being easy for the effect of a base material to come out is, so that the punctiform failure which is the effectiveness of this invention generally increases with increase of desiccation thickness and desiccation thickness increases.

[0050] it asks for the minute irregularity with the aforementioned short wavelength by measuring on conditions

without being a measurement machine like the above and performing a high region cut-off — having (for example, approach indicated by JIS-B -0601) — all irregularity with short wavelength is also measured in this case.

[0051] Although the effectiveness of this invention can be acquired if the conditions of the above-mentioned external waviness are contained within the limits of this invention, when a component with the above-mentioned short wavelength is put in and measured, it is desirable that the maximum height per [ which is called for according to JIS-B -0601 ] criteria die length of 2.5mm is 6 micrometers or less, and especially 4 micrometers or less are the most desirable.

[0052] Next, especially the paper base material that covered both sides with the polyolefine used preferably is explained.

[0053] The stencil paper used for a paper base material uses wood pulp as the main raw material, and, in addition to wood pulp, paper making is carried out using synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, if needed. Although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used as wood pulp, it is desirable to use more many [ for a staple fiber ] LBKP, NBSP(s), LBSP(s), and NDP (s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0054] The pulp of the above-mentioned pulp which chemical pulp with few impurities (sulfate pulp and sulfite pulp) was used preferably, and performed bleaching processing, and raised the whiteness degree is also useful. [0055] Hara Kaminaka can add suitably flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc.

[0056] The freshness of the pulp used for paper making has desirable 200-500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of 24-mesh residue weight % and weight % of the 42-mesh residue as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0057] The basis weight of stencil paper has 60 thru/or desirable 250g, and 90 thru/or especially its 200g are desirable. The thickness of stencil paper has 50 thru/or desirable 250 micrometers.

[0058] After a paper-making phase or paper making, calender processing of the stencil paper can be carried out, and it can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m2 (JIS-P-8118). Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P-8143.

[0059] A surface sizing compound may be applied to a stencil paper front face, and the sizing compound which can be added to said Hara Kaminaka as a surface sizing compound, and the same sizing compound can be used. [0060] When the hot water extraction method specified by JIS-P -8113 is resembled and it is measured more, pH of stencil paper can use a part of other LLDPE(s) (line low density polyethylene), polypropylene, etc., although polyethylene is desirable and is mainly the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density especially as polyolefine with which that it is 5-9 cover a desirable stencil paper front face and a desirable rear face.

[0061] As for especially the polyethylene layer by the side of an ink absorbing layer, what added the titanium oxide of a rutile or an anatase mold in polyethylene as widely performed by the printing paper for photographs, and improved opacity and a whiteness degree is desirable. A titanium oxide content is 5 - 15% of the weight preferably three to 20% of the weight in general to polyethylene.

[0062] After preparing an ink absorbing layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is damp and range whose 20-50-micrometer and back layer side the polyethylene layer by the side of an ink absorbing layer is 10-40 micrometers in general, although it is chosen so that the curl by highly-humid-izing may be optimized.

[0063] Furthermore, as for the above-mentioned polyethylene covering paper base material, it is desirable to have the following properties.

[0064] \*\* It is desirable that a lengthwise direction is [2 thru/or 30 kg, and a longitudinal direction ] 1 thru/or 20 kg by the reinforcement specified by :JIS-P -8113 in hauling strength.

[0065] \*\* 10 thru/or 300g, and a longitudinal direction have [ tear reinforcement / a lengthwise direction ] 20 thru/or desirable 400g by the convention approach by JIS-P -8116.

[0066] \*\* Clerks stiffness: 20-400g/100 are desirable.

[0067] \*\* Compressibility  $\geq$ =103 kgf/cm2\*\* surface smoothness : especially 1000 seconds or more have the desirable Beck smoothness specified to JIS-P -8119 500 seconds or more.

[0068] \*\* Surface glossiness: when it measures at the include angle of 75 degrees by the approach specified to JISZ-8741, it is 90% or more especially preferably 70% or more preferably 30% or more.

[0069] \*\* Surface whiteness degree: when it measures by the approach indicated by JIS-Z -8722 and displays

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according to JIS-Z -8729, [0070]

[External Character 1]

L*は85%以上、特に90%以上が好ましい。また、(a*, b*) は

(-2, 2)、(4, 2)、(4, -8)および(-3, -8)で囲まれる範囲の色調が好ましい。
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[0071] \*\* Opacity : when it measures by the approach specified to JIS-P -8138, it is especially most preferably [ 94% or more of ] desirable 90% or more 50% or more.

[0072] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of a record layer for the purpose, such as to enlarge bond strength of the above—mentioned base material and a record layer.

[0073] In this invention, it has at least one layer of opening layers which contain a hydrophilic binder and a non-subtlety particle on a base material as a record layer.

[0074] Although a non-subtlety particle with a small particle size is desirable at a low refractive index, for example, a silica, colloidal silica, a calcium silicate, a calcium carbonate, a boehmite aluminum hydroxide, or its hydrate is raised as the above-mentioned inorganic particle, it is a silica preferably.

[0075] A silica particle is divided roughly into dry process and a wet method according to a manufacturing method, and the approach by the gaseous-phase method hydrolysis in the elevated temperature of silicon halide and the approach of carrying out heating hydride generation of silica sand and the corks with an arc process with an electric furnace, and smothering this are learned as a dry-process particle silica. Moreover, after the acidolysis of silicate generates active silica as a wet method silica, carry out a polymerization moderately, and it is made to condense and precipitate, and is obtained.

[0076] The anhydrous silica compounded by the gaseous-phase method also in silica impalpable powder especially in this invention is desirable at the point that especially voidage and a strong film strength are obtained.

[0077] The mean particle diameter of the above-mentioned inorganic particle has a desirable thing 0.1 micrometers or less as the primary particle.

[0078] When a non-subtlety particle is a gaseous-phase method silica, the mean particle diameter of a primary particle is 0.003-0.03 micrometers, and 0.006-0.02 micrometers is especially the most desirable. Although the secondary gaseous-phase method silica is condensed in coating liquid and a bigger particle can be formed, the mean particle diameter of secondary floc has desirable 0.03-0.2 micrometers in this case.

[0079] In the above, the mean particle diameter of a non-subtlety particle observes the cross section and front face of the particle itself or an opening layer with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle size of the particle of 100 arbitration. The particle size of each [ here ] is expressed with the diameter when assuming a circle equal to the projected area. [0080] In the record form of this invention, as a hydrophilic binder used combining the above-mentioned inorganic particle, although polyvinyl alcohol and its derivative, polyalkylene oxide, a polyvinyl pyrrolidone, polyacrylamide, gelatin, hydroxyl ethyl cellulose, carboxyl methyl cellulose, a pullulan, casein, a dextran, etc. can be used, it is desirable from the point of the film strength immediately after printing that the bloating tendency and the solubility over the high-boiling point organic solvent and water which ink contains use a low hydrophilic binder.

[0081] In especially this invention, polyvinyl alcohol or its derivative is desirable, and average degree of polymerization is [ average degree of polymerization ] 2000 or more polyvinyl alcohol or a derivative of those most preferably 1000 or more especially. Moreover, whenever [ saponification / 70 - 100% of ] is desirable, and is especially the most desirable. [ 80 - 100% of ]

[0082] Although the above-mentioned hydrophilic binder can also be used together two or more sorts, even if it is this case, it is desirable to contain polyvinyl alcohol or its derivative at least 50% of the weight or more. [0083] As the above-mentioned poly BIRUARUKORU derivative, cation denaturation polyvinyl alcohol, anion denaturation polyvinyl alcohol, or Nonion denaturation polyvinyl alcohol is raised.

[0084] Cation denaturation polyvinyl alcohol is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0085] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-(- methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0086] the ratio of the cation denaturation radical content monomer of cation denaturation polyvinyl alcohol — vinyl acetate — receiving — 0.1–10-mol % — it is 0.2–5-mol % preferably.

[0087] the polymerization degree of cation denaturation polyvinyl alcohol — usually — 500-4000 — 1000-4000

are preferably desirable.

[0088] whenever [ moreover, / saponification / of a vinyl acetate radical ] — usually — 60-100-mol % — it is 70-99-mol % preferably.

[0089] The copolymer of the polyvinyl alcohol and JP,61–237681,A which have an anionic radical anion denaturation polyvinyl alcohol is indicated to be by JP,1–206088,A and vinyl alcohol which is indicated by the 63–307979 official report, and the vinyl compound which has a water–soluble radical, and the denaturation polyvinyl alcohol which has a water–soluble radical which is indicated by JP,7–285265,A are mentioned. [0090] Moreover, the polyvinyl alcohol derivative which added a polyalkylene oxide radical which is indicated by JP,7–9758,A to a part of vinyl alcohol as Nonion denaturation polyvinyl alcohol, for example, the block copolymer of the vinyl compound and vinyl alcohol which have the hydrophobic radical indicated by JP,8–25795,A, etc. are mentioned.

[0091] The ratio of the non-subtlety particle to the hydrophilic binder of the opening layer of the record form of this invention needs to be 5 or more times in a weight ratio, when obtaining high voidage and a high film strength. In being less than 5 times, the reinforcement of a coat tends to fall with the high-boiling point organic solvent as for which voidage falls and sufficient ink absorption capacity becomes is hard to be obtained and which remains in a hydrophilic binder after ink jet record. The ratio to the hydrophilic binder of a desirable non-subtlety particle is six or more.

[0092] The upper limit of the ratio of the non-subtlety particle to a hydrophilic binder is 20 or less in general from the crack engine performance of a coat.

[0093] It is desirable to add the hardening agent which can construct a bridge with said hydrophilic binder into the opening layer of the record form of this invention at the point of improving the film strength after printing which is amelioration of the film formation nature of an opening layer, the water resisting property of a coat, and the purpose of this invention. Inorganic hardening agents, such as an organic hardening agent which contains an epoxy group, an ethylene imino group, an activity vinyl group, etc. as such a hardening agent, chromium alum, a way acid, or way sand, are mentioned.

[0094] Especially when a hydrophilic binder is polyvinyl alcohol, the epoxy system hardening agent which has at least two epoxy groups in a molecule, a way acid or its salt, and way sand are desirable. As a way acid, not only an alt.way acid but a meta-way acid, a way [ degree ] acid, etc. can be used.

[0095] 1-200mg per above-mentioned binder [ hydrophilic ] 1g of additions of the above-mentioned hardening agent is 2-100mg preferably.

[0096] Various kinds of additives can be made to contain if needed in the layer of the arbitration by the side of the ink receptiveness layer of the ink jet record form of this invention.

[0097] For example, an ultraviolet ray absorbent given in JP,57–74193,A, a 57–87988 official report, and a 62–261476 official report, JP,57–74192,A, a 57–87989 official report, a 60–72785 official report, The fading inhibitor indicated by a 61–146591 official report, JP,1–95091,A, the 3–13376 official report, etc., An anion, a cation or the various surfactants of Nonion, JP,59–42993,A, The fluorescent brightener indicated by a 59–52689 official report, a 62–280069 official report, a 61–242871 official report, JP,4–219266,A, etc., Various well–known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, an acetic acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0098] Into the configuration layer of the arbitration by the side of the ink absorptivity of the record form of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,4-15744,B, JP,61-58788,A, and a 62-174184 official report, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0099] The amount of the spreading solid content by the side of the ink recording surface in the ink jet record form of this invention has in general desirable 5-40 g/m2, and its 10-30 g/m2 is more desirable.

[0100] When using the record form of this invention as a record form for ink jets, it is [ 1m of record forms ] desirable as void volume to be adjusted to the range preferably set to 15-30ml 10-40ml per two.

[0101] However, void volume is J.TAPPI. Paper pulp test method When the ink absorptivity side of a record form is measured by the approach indicated by the liquid absorptivity test method (Bristow law) of No.51 -87 paper and the paper board, absorption time amount is expressed with the amount of liquid transition in 2 seconds (ml/m2). In addition, although the liquid used at this time is pure water (ion exchange water), in order to make distinction of measurement area easy, less than 2% of water soluble dye may be contained.

[0102] The record form of this invention may have the record layer which has the above mentioned opening layer more than two-layer, and the ratios to the hydrophilic binder of the non-subtlety particle of the opening layer more than two-layer may differ in each other in this case.

[0103] Moreover, in addition to the above-mentioned opening layer, it may not have an opening layer but you may have the layer of bloating tendency to ink.

[0104] Such a swelling layer may be prepared in the upper layer (side which is separated from a base material) of the lower layer (side near a base material) of an opening layer, or an opening layer, and when there is an opening layer more than two-layer further, it may be prepared between opening layers. As an example of the hydrophilic binder which a hydrophilic binder is usually used for this bloating tendency layer, and is used here, the hydrophilic binder used for said opening layer is mentioned.

[0105] In order to adhere at the time of piling up immediately after curl prevention or printing to the opposite side and to raise a \*\* ink imprint further, as for the side which has the ink absorptivity layer of the record form of this invention, it is desirable to prepare the back layer of various classes.

[0106] Although the configuration of a back layer changes also with the class of base material, thickness, and the configuration and thickness of an ink absorptivity layer, generally a hydrophilic binder and a hydrophobic binder are used. The range of the thickness of a back layer is usually 0.1–10 micrometers.

[0107] Moreover, it adheres to a back layer as other record forms, and-izing of the front face can be carried out [ split face ] to prevention, note nature amelioration, and a pan for conveyance nature amelioration within an ink jet recording device. The organic or inorganic particle whose particle size is 2-20 micrometers is preferably used for this purpose.

[0108] Next, how to manufacture the record form of this invention is explained.

[0109] On a base material, the record form of this invention carries out spreading desiccation of the record layer which has an opening layer at least, and is obtained. The coating liquid (said additive added suitably a hydrophilic binder, a non-subtlety particle, and if needed is contained) which forms an opening layer is applied on a base material, and although it dries, if the temperature of coating liquid is dried after the thing of the range of 30–50 degrees C is usually used and it makes it once cool after applying on a base material, the punctiform failure at the time of desiccation will be mitigated in this case.

[0110] By once cooling coating liquid, the viscosity of coating liquid increases remarkably, the fluidity of a paint film falls and the nonuniformity of the paint film under the vibration at the time of conveyance or the effect of a wind decreases sharply. When there is nonuniformity of a paint film, punctiform failure in the part where thickness increased not only increases, but partially, nonuniformity arises in void volume and there is [ whether it is a lifting and ] nothing to it about the serious effect for image quality.

[0111] From the temperature of coating liquid, the temperature of a paint film is preferably reduced by 20 degrees C or more, and evaporates 10 degrees C or more of a part of moisture and low-boiling point organic solvents in the condition. If this condition is reached, in order for the viscosity of a paint film to increase much more quickly and to approach a gelation condition, when it passes over this, even if it makes drying temperature increase, a paint film stops moving, and even if it dries a hot wind quickly [ delivery ], a good paint film side without nonuniformity or punctiform failure is acquired.

[0112] the once cooled temperature — the particle size of the non-subtlety particle of coating liquid, concentration, the class of hydrophilic binder and concentration, and the class of hardening agent and an amount — although it may change by various factors, such as an interaction of a non-subtlety particle and a hydrophilic binder, 0–20 degrees C is usually 5–15 degrees C preferably.

[0113] Although a cooldown delay may change by cooling temperature, humid thickness, etc., it is usually 10 - 60 seconds preferably for 5 to 200 seconds.

[0114] As for the desiccation after cooling, it is desirable to usually mention drying temperature gradually. Usually, finally it dries by 40–60–degree C warm air after fixed time amount desiccation at the temperature near a room temperature.

[0115] Because of the above-mentioned purpose, especially the viscosity property of coating liquid is important. It is coating liquid of 5 - 500cp extent at spreading temperature preferably, and at the time of cooling, 1000 or more cp is adjusted so that it may grow into a gelation condition preferably especially.

[0116] It is desirable to make it the viscosity ratio of coating liquid temperature and the temperature at the time of cooling become 100 or more times especially.

[0117] The approach of applying the above-mentioned opening layer on a base material can be suitably chosen from a well-known approach, and can be performed. As a spreading method, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain method of application, or given in a U.S. Pat. No. 2,681,294 official report is used preferably. [0118] Next, the record form of this invention is explained below about the water color ink in the case of using it as an ink jet record form.

[0119] Water color ink is usually water soluble dye and a solvent object, and a record liquid that consists of other additives. Although water soluble dye, such as direct dye well-known as water soluble dye at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0120] Although it becomes as a subject, when liquid ink dries water, in order that a color may deposit and the solvent of water color ink may prevent the blinding in a nozzle tip or an ink supply path, a high-boiling point organic solvent with the boiling point liquefied above about 120 degrees C is usually used at a room temperature.

A high-boiling point organic solvent needs to have a high miscibility to water, while it is required that it should have vapor pressure far lower than water, since it has the operation which formed elements, such as a color, deposit and prevents generating of a big and rough sludge when water evaporates.

[0121] Although many organic solvents of a high-boiling point are usually used as a high-boiling point organic solvent for such the purpose As an example, ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the JICHIREN glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, Alcohols, such as 1, 2, 4-pentanetriol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, and a polyethylene glycol (average molecular weight is about 300 or less), are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0122] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, triethanolamine, and the triethylene glycol monobutyl ether etc. is desirable.

[0123] As an additive of others which water color ink contains, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rusrproofer, etc. are mentioned, for example.

[0124] Water-color-ink liquid is the purpose which stabilizes the regurgitation from an ink jet nozzle in order to make wettability to a record form good, and in 25 degrees C, it is desirable to have the surface tension of 28 -40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0125] Moreover, the viscosity of water color ink is usually 2.5 - 5cp preferably two to 8 cp in 25 degrees C.

[0126] The range of pH of water color ink is usually 4-10.

[0127] Since the diameter of the minimum dot with a diameter of about 20–60 micrometers is obtained in the record paper as a minimum liquid ink drop breathed out from an ink nozzle in the case of the capacity of 1-30x10-3nl, it is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. It is the case where the drop which has the volume of 2-20x10-3nl preferably is breathed out as the minimum drop. [0128] Moreover, in the method recorded about a Magenta and cyanogen at least in the ink whose concentration is two kinds from which said water color ink differs more than twice respectively, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but this invention can be applied, also when this recording method is adopted.

[0129] In the ink jet record approach, as the record approach, various kinds of well-known methods can be used conventionally, and the detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique. [0130] In the ink jet record approach of this invention, combining suitably approaches, such as making [ many /

as possible ] thickness for the void volume of the record form which lessens the amount of maximum regurgitation ink as much as possible which lowers the ratio in the ink of a high-boiling point organic solvent, the approach of making void volume to the amount of high-boiling point organic solvents in the amount of the maximum ink 3 or more times sets up the optimal conditions, and is chosen.

[0131] As mentioned above, although the record form of this invention has been explained as a record form for ink jets the record form of this invention — except for ink jet record — a thermal-ink-transfer-printing method (the so-called melting mold hot printing method which is made to heat and carry out melting of the record ingredient containing the ink of thermofusion nature from an ink sheet base material side, and is made to record ---) And it is applicable also to record forms, such as a record form for the so-called sublimation mold hot printing methods which heats like the record ingredient melting mold hot printing method which consists of a sublimation mold color and high softening-degree resin, and is recorded, and an electrophotography method.

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## **EXAMPLE**

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples.

[0133] The paper base material which covered both sides of 1160g of examples/, and the stencil paper for photographs of m2 with polyethylene (an anatase mold titanium dioxide is contained 13% of the weight in a polyethylene layer with a thickness [ by the side of a recording surface ] of 40 micrometers.) the back layer which the thickness of the polyethylene layer by the side of a rear face makes solid content the Tg=65 degree C diameter latex resin of an acrylic on a polyethylene layer by 25 micrometers, and is contained two times 0.3 g/m by making into a mat agent the silica 0.6g/m2, and whose mean diameter are about 13 micrometers — having — it prepared.

[0134] As a property of the above-mentioned polyethylene covering paper, it asked for glossiness, WCM, and the maximum height (the criteria die length found according to JIS-0601 is the maximum height per 2.5mm, and mum unit), and was shown in Table 1.

[0135] Next, 150g of primary particle silica powder whose mean particle diameter is about 7nm was added in 1000ml of pure water, the high-speed homogenizer distributed, and pale clear dispersion liquid were obtained. Next, in this silica water dispersion (I), average degree of polymerization added gradually 2% polyvinyl alcohol water-solution (II) (ethyl acetate is contained 6% of the weight)1000ml whenever [ saponification / whose ] is 88% by 3500. Subsequently, 40ml of 4% way sand water solutions was added as a hardening agent, the high-speed homogenizer distributed, and white translucent-like coating liquid was obtained. This liquid contains the silica 7.5 times by the weight ratio to polyvinyl alcohol. Moreover, the viscosity of the above-mentioned coating liquid was 50,000cp when it measured by the Brookfield viscometer, and it measured at 60cp and 15 degrees C by 40 degrees C.

[0136] Subsequently, the 40-degree C coating liquid obtained as mentioned above was applied to the recording surface side of the above-mentioned polyethylene covering paper, and was made to once cool so that spreading coat temperature may turn to 15 degrees C or less (for 20 seconds). Subsequently, the 25-degree C wind was sprayed for the 20-degree C wind for 30 seconds, for 60 seconds and a 45 more-degree C wind were sprayed for 30 seconds and for a 35-degree C wind one by one for 120 seconds, it dried, 25 more degrees C and the ambient atmosphere of 50% of relative humidity were passed for 30 seconds, gas conditioning was carried out, and the record form -1 was produced.

[0137] Next, record form which covered the same polyethylene layer as the record form -1 on the front reverse side in the record form -1 using the various stencil paper with which smooth nature differs as stencil paper of a base material - 2-4 were produced like the record form -1. Record form - The optical property and smooth nature after polyethylene covering of 1-4 were shown in Table 1.

[0138] Record form – 1–4 were saved for three days at 39 degrees C by the condition of having wound in the shape of a roll, after spreading desiccation.

[0139] It evaluated about the following items [ form / which was obtained / record ].

[0140] (1) Void volume Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used, and the amount of transition for [ contact time ] 2 seconds (ml/m2) was calculated as void volume. [0141] (2) Contact time calculated ink absorptivity from the amount of transition in 0.5 seconds (ml/m2) using the same testing machine as having measured ink absorptivity void volume.

[0142] (3) The specular gloss was measured 75 degrees with the deflection photometer (VGS-101DP) by glossiness Nippon Denshoku Industries Co., Ltd.

[0143] (4) The surface punctiform defective number was investigated about the spreading sample of 10x10cm of failure defects.

[0144] (5) After 23 degrees C and relative humidity saved at 80% after solid printing for 24 hours by the ink jet printer by film strength Seiko Epson, Inc., and MJ-5100C, it scratched in the same environment, the tip applied the continuation load (0-100g) to the sapphire needle of 0.3mmphi using the strength test machine (Hayden try BOGIA, new east science incorporated company make), the film strength was examined, and reinforcement by which a coat is destroyed was made into the film strength.

[0145] If it is 30g or more in general by this evaluation approach, it can be said that it has the practically sufficiently high film strength.

[0146] In addition, in (1) and (2), the used ink used the ink which contains a water-soluble Magenta color for a diethylene glycol 1% of the weight 20% of the weight. A result is shown in Table 1.
[0147]

[Table 1]

記録用紙	支持体 <b>の特性</b> 用 紙		記録層	記録用紙の特性						
	光沢度	Wcm	最大高さ	無機微粒子/	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度
記録用紙-1 (本発明) 記録用紙-2 (本発明) 記錄用紙-3 (本発明) 記録用紙-4 (比較例)	94% 93% 91% 90%	1.2µm 2.3µm 3.5µm 5.2µm	1.9µm 4.1µm 5.2µm 6.3µm	7.5 7.5 7.5 7.5	38 µm 38 µm 38 µm 38 µm	24mi 24mi 24mi 24mi	16m1 16m1 16m1 16m1	61% 61% 61% 53%	0 1 12 >100	729 699 709 739

[0148] Record form whose WCM is 4 micrometers or less when changing the class of stencil paper and changing the surface characteristic after covering from the result of Table 1 with polyethylene resin – 1–3 are understood that there are few failure defects compared with the record form –4 with which WCM exceeds 4 micrometers. [0149] When especially WCM uses the base material which is 2 micrometers or less, a failure defect is desirable at 0.

[0150] Moreover, according to the difference of a base material, void volume and ink absorptivity are hardly influenced, but desiccation thickness is 30 micrometers or more, and since it has high voidage (about 63%), void volume almost sufficient by the usual ink jet record is held.

[0151] The coating liquid which forms the opening layer which prepared the polyethylene covering paper base material to which the thickness of the polyethylene layer by the side of a recording surface was changed in the record form -1 produced in the example 2 example 1 as shown in Table 2, and was produced in the example 1 is applied like an example 1, and it is a record form. - 21-24 were produced. Record form with which various clearing-up processings are performed for a front face immediately after painting the polyethylene layer on a side front in the Hara paper, and surface characteristics differ on the other hand in the record form -1 produced in the example 1 - 25-27 were produced like the record form -1.

[0152] The die length of a pitch in which the base material of the record form -25 is called the so-called silky surface is clearing up of hundreds of micrometer unit, and that of the base material of the record form -27 is the detailed mat side where clearing up is called the so-called mat side. The record forms -26 are these middle. [0153] Furthermore, the base material of the record form -28 processes and split-face-izes the support surface of the record form -1 with a 40-degree C acetone solution. Usually, effectiveness is in the increase of an adhesive property [be / they / these split faces] of a base material and a record layer.

[0154] Record form – The property after applying the surface characteristic and record layer of polyethylene covering paper of 21–28 was evaluated like the example 1. A result is shown in Table 2. [0155]

[Table 2]

記録用紙	ポリエチレ	ン層	支持体の特性			記録層	記録用紙の特性		
	厚み (μm)	片付け	光沢度	Wcm	最大高さ	無機效粒子/ 親水性パインター	光沢度	故障欠陥	皮膜強度
記録用紙-21(本発明)	30 µ m	無	92%	1.7µm	2.1 µ m	7.5	59%	0	71 g
記録用紙-22(本発明)	20 µ m	無	85%	2.5µm	3.4 µ m	7.5	58%	2	70 g
記錄用紙-23(本発明)	15 µ m	<b>2</b> ##	71%	3. 2 $\mu$ m	5. 2 µ m	7.5	58%	10	73 g
記録用紙-24(比較例)	10 µ m	無	56%	4.7µm	7.1µm	7.5	51%	90	68 g
記録用紙-25(比較例)	40 µ m	有	46%	5.8 µ m	7.8µm	7. 5	50%	>100	44 g
記錄用紙-26(比較例)	40 µ m	有	9%	4.6μm	6.3 µ m	7. 5	36%	>100	68 g
記錄用紙-27(本発明)	40 µ m	有	5%	3.3 µ m	3. 2 µ m	7.5	41%	. 8	67 g
記錄用紙-28(本発明)	40 µ m	粗面化	18%	2.3µm	3.1 µ m	7.5	53%	3	68 g

[0156] Record form of this invention the result of Table 2 to whose WCM is 4 micrometers or less - 21, 22, and 23 are understood that there are few failure defects as compared with the comparative record form -24. Moreover, it turns out that WCM is excellent in the record form -21 2 micrometers or less especially especially like an example 1.

[0157] Record form whose WCM is 4 micrometers or less even if it is the case where tidied up and processed the front face of a polyethylene resin layer, or split-face-ized on the other hand, and the glossiness of a base material uses a low thing - 27 and 28 are understood that there are few failure defects. Moreover, when WCM exceeds 4 micrometers also in a clearing-up base material, it turns out that a failure defect increases quickly. [0158] Record form which has desiccation thickness as humid thickness is changed and shows the coating liquid produced in the example 1 on the polyethylene covering paper base material for record form-4 produced in the example of comparison 1 example 1 in Table 3 - 31-34 were produced like the record form -4.

[0159] The result which estimates as an example 1 similarly and is shown in Table 3 was obtained. [0160]

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記録用紙	支持体の特性	記録層 無機磁粒子/		記 錄	用紙の!	—— 寺 性	
	WcH	親水性バインダー	乾燥膜厚	量容期空	インク吸収性	光沢度	故障欠陥
記録用紙-31(比較例) 記録用紙-32(比較例) 記録用紙-33(比較例) 記録用紙-34(比較例)	5. 2μm 5. 2μm 5. 2μm 5. 2μm	7.5 7.5 7.5 7.5	45 μ m 30 μ m 25 μ m 20 μ m	29m1 19mi 16m1 12m1	21 m l 1 l m l 7 m l 4 m l	52% 51% 62% 64%	>100 >100 58 20

[0161] Since void volume falls gradually in connection with this although a failure defect will fall if desiccation thickness is decreased even if WCM uses the base material exceeding 4 micrometers from the result of Table 3, it is a record form. - 31-34 cannot be used practical.

[0162] Record form produced in the example 3 example 1 - It is a record form except having changed the particle silica into the gaseous-phase method [ the mean particle diameter of a primary particle is about 20nm ] silica in 1-4. - It is a record form like 1-4. - 41-44 were produced. It was similarly estimated as the example 1 and the result shown in Table 4 was obtained. [0163]

[Table 4]

記録用紙	支持体の特性	記録 暦 無機微粒子/		. 25	おけい はい					
	W <sub>c∎</sub>	•	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度		
記錄用紙-41(本発明) 記錄用紙-42(本発明) 記錄用紙-43(本発明) 記錄用紙-44(比較例)	1.2µm 2.3µm 3.5µm 5.2µm	7. 5 7. 5 7. 5 7. 5	38 µ m 38 µ m 38 µ m 38 µ m	26m1 26m1 26m1 26m1	19m I 19m I 19m I 19m I	54% 52% 51% 51%	0 3 15 >100	60 g 57 g 58 g 53 g		

[0164] The result of Table 4 shows that the same effectiveness as an example 1 is acquired. However, the glossiness of a recording surface falls with increase of the particle size of the primary particle of a silica more slightly than an example 1, and void volume is increasing a little.

[0165] 150g of primary particle silica powder whose example of comparison 2 mean particle diameter is about 7nm was added in 1000ml of pure water, the high-speed homogenizer distributed, and pale clear dispersion liquid were obtained. Next, in this silica water dispersion (I), average degree of polymerization added gradually 2% polyvinyl alcohol water-solution (II) (ethyl acetate is contained 6% of the weight)2000ml whenever [ saponification / whose ] is 88% by 3500. Subsequently, 40ml of 4% way sand water solutions was added as a hardening agent, the high-speed homogenizer distributed, and white translucent-like coating liquid was obtained. This liquid contains the silica 3.75 times by the weight ratio to polyvinyl alcohol.

[0166] Record form used in the example 1 – With the polyethylene of 1–4, it applies in the covering paper so that desiccation thickness may become being the same as that of an example 1 about the above-mentioned coating liquid, and humid thickness may be set to 170 micrometers, and it dries by the approach indicated by the example 1, and is a record form. – 51–54 were produced. It was similarly estimated as the example 1 and the result shown in Table 5 was obtained.

[0167] [Table 5]

記録用紙	支持体の特性	記 録 層無機微粒子/	記録用紙の特性								
	Wcn		乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度			
記録用紙-51(比較明) 記録用紙-52(比較明) 記録用紙-53(比較明) 記録用紙-54(比較例)	1. 2 µm 2. 3 µm 3. 5 µm 5. 2 µm	3. 75 3. 75 3. 75 3. 75	38 µ m 38 µ m 38 µ m 38 µ m	15m1 15m1 15m1 15m1	4m l 4m l 4m l 4m l	81 % 80 % 80 % 78 %	0 0 0 3	17g 15g 15g 14g			

[0168] Although a failure defect is hardly produced from the result shown in Table 5 even if WCM uses the thing exceeding 4 micrometers as a base material when the ratio to the hydrophilic binder of a non-subtlety particle is made or less into five, but the glossiness of a recording surface is also very high, it turns out that void volume falls and the reinforcement of a coat falls greatly.

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### (54) 【発明の名称】 記録用紙およびその製造方法

#### (57)【要約】

【課題】 高インク吸収性、高光沢性、高途膜強度を有し、しかも点状故障を大きく減少させた記録用紙の提供。

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【特許請求の範囲】

【請求項1】 支持体上に、親水性バインダーと無機微粒子を含有する空隙を持つ記録層を少なくとも1層有し、該記録層の親水性バインダーに対する無機微粒子の比率が重量比で5倍以上である記録用紙において、該支持体の記録層側の表面特性が、JIS-B-0610に従って測定された断面曲線からカットオフ値0.8mmの条件で導かれる遮波うねり曲線について基準長さ2.5mmとして濾波最大うねりを測定したときに、最大うねりが $4\mu$ m以下であることを特徴とする記録用紙。

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【請求項2】 前記記録層の乾燥膜厚が30μm以上であることを特徴とする請求項1記載の記録用紙、

【請求項3】 前記記録層の表面の光沢度が、JIS-Z-8741に規定された75度鏡面光沢度が50%以上であることを特徴とする請求項1または2記載の記録用紙。

【請求項4】 前記無機微粒子が平均粒径が0.03~0.003μmの平均1次粒子径を有する気相法により合成された微粒子シリカであることを特徴とする請求項1~3のいずれか1項に記載の記録用紙。

【請求項5】 前記親水性バインダーがポリビニルアルコールまたはその誘導体であることを特徴とする請求項1~4のいずれか1項に記載の記録用紙。

【請求項6】 前記記録層が親水性バインダーを架橋し得る硬膜剤を含有することを特徴とする請求項1~5のいずれか1項に記載の記録用紙。

【請求項7】 前記支持体が原紙の両面をプラスチック 樹脂で被覆した紙支持体であることを特徴とする請求項 1~6のいずれか1項に記載の記録用紙。

【請求項8】 記録用紙が水溶性インクで記録可能なインクジェット記録用紙であることを特徴とする請求項1~7のいずれか1項に記載の記録用紙。

【請求項9】 支持体上に、親水性バインダーと無機微粒子を含有する空隙を持つ記録層を少なくとも1層有し、該記録層の親水性バインダーに対する無機微粒子の比率が重量比で5倍以上であって、該支持体の記録層側の表面特性が、JIS-B-0610に従って測定された断面曲線からカットオフ値0.8mmの条件で導かれる濾波うねり曲線について基準長さ2.5mmとして濾波最大うねりを測定したときに、最大うねりが4μm以下である記録用紙の製造方法において、該記録層を形成する塗布液を前記支持体上に塗布した後に、一旦冷却してから乾燥することを特徴とする記録用紙の製造方法。

#### 【発明の詳細な説明】

#### [0001]

【発明の属する技術分野】本発明は、色材を用いて画像を記録する記録用紙に関し、特にインクジェット記録において高いインク吸収性、高光沢性および高い皮膜の強度を有し、しかも皮膜の欠陥の少ない記録用紙とその製造方法に関する。

[0002]

【従来の技術】インクジェット記録は、インクの微小液 滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものである が、比較的高速、低騒音、多色化が容易である等の利点 を有している。この方式で従来から問題となっていたノ ズルの目詰まりとメンテナンスについては、インクおよ び装置の両面から改良が進み、現在では各種プリンタ ー、ファクシミリ、コンピューター端末等、さまざまな 分野に急速に普及している。

【0003】その詳細は例えば、インクジェット記録技 術の動向(中村孝一編、平成7年3月31日、日本科学 情報株式会社発行)に記載されている。

【0004】このインクジェット記録方式で使用される記録用紙としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合に於いてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでぼやけないこと等が一般的には要求されている。

【0005】インクジェット記録用紙としては従来から 種々の記録用紙が用いられている。例えば、普通紙、紙 支持体上に親水性バインダーと無機顔料から成る層を塗 設した各種の塗工紙(アート紙、コート紙、キャストコ ート紙等)、更にはこれらの紙、透明または不透明の各 種のプラスチックフィルム支持体あるいは紙の両面をプ ラスチック樹脂で被覆した各種の支持体上に記録層とし てインク吸収性層を塗設した記録用紙が用いられてい る。

【0006】上記インク吸収性層としては、親水性バインダーを主体に構成されるいわゆる膨潤型のインク吸収性層と、空隙層を記録層中に持つ空隙型のインク吸収層に大きく分けられる。

【0007】膨潤型インク吸収性層の利点はインク溶媒 (水及び高沸点有機溶媒)が完全に蒸発した後では非常 に高い光沢性と高い最高濃度が得られる点にあるが、反 面、インク吸収速度が後述する空隙型記録用紙に比べて 遅く、高インク領域でビーディング等を起こしてザラツ キの発生による画質が低下しやすい問題があり、更にイ ンク溶媒、特に高沸点有機溶媒の蒸発が極めて遅いため に印字後しばらくは親水性バインダー中に高沸点有機溶 媒が残存して親水性バインダーが膨潤した湿潤状態に長 期間置かれることに伴う問題がある。

【0008】具体的には印字後数時間、場合により数日間は印字表面を強く擦ったり紙などを重ねることができない状況にある。

【0009】一方、空隙型のインク吸収性層は、記録層中に空隙を有するために高いインク吸収性を示す。このため、膨潤型に比較して高インク領域における画像のビーディングが起こりにくく高濃度域において画質の劣化

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が少ない。

【0010】また、空隙型のインク吸収性層は空隙容量がインク量に対して十分あれば、空隙構造中に有機溶媒が残存していたとしても、少なくとも表面は印字直後に見かけ上乾いた状態になり、表面に触れたりプリント同士を重ね合わせること等も一応可能となる。

【0011】この種のインク吸収性層としては、比較的透明性の高い層が形成される点から低屈折率(特に約1.6以下の屈折率が好ましい)でしかも粒径の小さな微粒子(特に200nm以下が好ましい)が好ましく用いられ、中でもかかる条件を満たすシリカ微粒子が空隙を効率良く形成し、しかも比較的高い光沢性が得られ、高い最高濃度の画像が得られることなどから特に好ましく用いられる。

【0012】そのような粒径の小さな無機微粒子をイン クジェット記録用紙に使用する従来技術として、例え ば、特開昭57-14091号、同60-219083 号、同60-219084号、特開平2-274857 号、同4-93284号、同5-51470、同7-1 79029号、同7-137431号、同8-2580 0号、同8-67064号および同8-118790号 等の各公報に記載されているコロイダルシリカ、特公平 3-56552号、特開昭63-170074号、特開 平2-113986号、同2-187383号、同7-276789号、同8-34160号、同8-1327 28号、及び8-174992号の各公報に記載されて いる気相法により合成された微粒子シリカ、例えば特公 平3-24906号、同3-24907号、同6-98 844号、同7-2430号、同121609号、特開 昭60-245588号、特開平2-43083号、同 30 2-198889号、同2-263683号、同8-1 12964号、同8-197832号および同8-25 8397号等に記載されている多孔質アルミナまたはそ の水和物、例えば、特開昭57-120486号、同5 7-129778号、同58-55283号、同61-20792号、同63-57277号、特開平4-25 0091号、同3-251487号、同4-25009 1号、同4-260092号および同7-40648号 等に記載された微粒子炭酸カルシウム等が挙げられる。

【0013】上記空隙型のインク吸収層を支持体上に有する記録用紙は、特に高い光沢性、高空隙率、高い最高濃度が得られる点で優れており、しかも比較的高い平面性の支持体を使用した場合に高い光沢面を持つ記録用紙が得られる。

【0014】そして、空隙層の親水性バインダーに対する無機微粒子の重量比を増加させるほど空隙率が上昇し、より少ない塗布量で良好なインク吸収性が達成しやすくなるが、一方で、皮膜の柔軟性が低下し、塗布面に微少のひび割れが生じやすくなる。特に親水性バインダーに対して無機微粒子の比率が重量比で5倍を超えると50

この問題が顕著に成りやすい。

【0015】このひび割れは、親水性バインダーと架橋 し得る硬膜剤を添加することで大きく改善されるが、点 状の塗布面の欠陥が僅かではあるが依然として残る問題 があった。この原因について種々検討を行った結果、こ の問題は空隙層の剛性と、支持体表面の平面性が関係し ていることがわかった。

【0016】すなわち、空隙層の塗布後の乾燥時に皮膜が収縮する過程で、皮膜は徐々に固い皮膜となっていくが、この時の皮膜の剛性が高すぎるために、支持体表面の微少なうねりや凹凸により局所的に皮膜に微小なクラックが入るためであることがわかった。

【0017】上記の問題点は皮膜が実質的に親水性バインダーからなる記録層を塗布する場合や、無機微粒子を使用した場合であっても、親水性バインダーに対して5重量%未満の場合にはあまり大きな問題になりにくい。

【0018】上記問題は乾燥過程で塗布面の乾燥速度の局所的なムラが生じやすい場合にいっそう発生しやすく、また、無機微粒子として平均1次粒径が100nm以下の微粒子を主体として使用し、高い平滑度を有し高光沢の記録面を有する記録用紙でいっそう起きやすいことも判明した。

【0019】前記特開平8-174992号には鏡面光 沢度が80%以上のポリオレフィン被覆紙支持体上に、 平均粒径が10nm以下の無機微粒子と親水性バインダ ーを使用し、高い光沢度を得るインクジェット記録用紙 が記載されている。しかしながら、単に支持体表面の光 沢度を規定しただけでは必ずしも上記課題は解決されない。

[0020]

【発明が解決しようとする課題】本発明は上記の実態に 鑑みてなされたものであって、本発明が解決しようとす る課題は、支持体上に空隙層を記録層として有する記録 用紙の製造の際の塗布面の点状故障やひび割れを改良 し、高いインク吸収性、光沢性、および皮膜強度を有す る記録用紙とその製造方法を提供することにある。

[0021]

【課題を解決するための手段】本発明の上記目的は、下記構成により達成された。

【0022】(1) 支持体上に、親水性バインダーと 無機微粒子を含有する空隙を持つ記録層を少なくとも 1 層有し、該記録層の親水性バインダーに対する無機微粒子の比率が重量比で 5 倍以上である記録用紙において、 該支持体の記録層側の表面特性が、 JIS-B-0610に従って測定された断面曲線からカットオフ値0.8 mmの条件で導かれる濾波うねり曲線について基準長さ 2.5 mmとして濾波最大うねりを測定したときに、最大うねりが  $4\mu$  m以下であることを特徴とする記録用紙、

【0023】(2) 前記記録層の乾燥膜厚が30μm

以上であることを特徴とする前記1記載の記録用紙。

【0024】(3) 前記記録層の表面の光沢度が、JIS-Z-8741に規定された75度鏡面光沢度が50%以上であることを特徴とする前記1または2記載の記録用紙。

【0025】 (4) 前記無機微粒子が平均粒径が $0.03\sim0.003\mu$ mの平均1次粒子径を有する気相法により合成された微粒子シリカであることを特徴とする前記 $1\sim3$ のいずれか1項に記載の記録用紙。

【0026】(5) 前記親水性バインダーがポリビニルアルコールまたはその誘導体であることを特徴とする前記1~4のいずれか1項に記載の記録用紙。

【0027】(6) 前記記録層が親水性バインダーを 架橋し得る硬膜剤を含有することを特徴とする前記1~ 5のいずれか1項に記載の記録用紙。

【0028】(7) 前記支持体が原紙の両面をプラス チック樹脂で被覆した紙支持体であることを特徴とする 前記1~6のいずれか1項に記載の記録用紙。

【0029】(8) 記録用紙が水溶性インクで記録可能なインクジェット記録用紙であることを特徴とする前記1~7のいずれか1項に記載の記録用紙

【0030】(9) 支持体上に、親水性バインダーと無機微粒子を含有する空隙を持つ記録層を少なくとも1層有し、該記録層の親水性バインダーに対する無機微粒子の比率が重量比で5倍以上であって、該支持体の記録層側の表面特性が、JIS-B-0610に従って測定された断面曲線からカットオフ値0.8 mmの条件で導かれる濾波うねり曲線について基準長さ2.5 mmとして濾波最大うねりを測定したときに、最大うねりが4μm以下である記録用紙の製造方法において、該記録層を形成する塗布液を前記支持体上に塗布した後に、一旦冷却してから乾燥することを特徴とする記録用紙の製造方法。

【0031】以下本発明を詳細に説明する。本発明の記録用紙に用いられる支持体としては、普通紙、アート紙、コート紙、およびキャストコート紙等の紙支持体、プラスチックフィルムや両面をポリオレフィンで被覆した紙支持体、あるいはこれらの貼り合わせた複合支持体が用いられる。

【0032】プラスチックフィルム支持体としては、た 40 とえばポリエチレン、ポリプロピレン、ポリスチレン、ポリエチレンテレフタレート、ポリエチレンナフタレート、トリアセチルセルロース、ポリ塩化ビニル、ポリイミド、ポリカーボネート、セロファンなどのプラスチックフィルム支持体等が好ましい。

【0033】これらのプラスチックフィルムは透明なもの、半透明なものおよび不透明なものを用途に応じて適 宜使い分けることが出来る。

【0034】白色フィルムとする場合、少量の硫酸バリウム、酸化チタン、酸化亜鉛などの白色顔料をプラスチ 50

ックフィルム支持体に含有させて得られた支持体をその まま用いてもよく、また、透明なフィルム支持体の裏面 側またはインク吸収性層側の支持体に近い側に白色顔料 (酸化チタン、硫酸バリウムなど)を有する層を設けた 支持体であっても良い。

【0035】また、両面をポリオレフィンで被覆した紙支持体としては従来カラー印画紙で通常用いられているポリエチレンで両面を被覆した紙支持体が好ましい。この場合、インク吸収性層側のポリエチレン樹脂層中にはアナターゼ型またはルチル型の酸化チタンをポリエチレンに対して7~15重量%含有させるのが、支持体の不透明度や白色度の向上、あるいは得られる画像の鮮鋭性を低下させないことから好ましい。

【0036】本発明においては、中でも両面をポリオレフィンで被覆した紙支持体を使用した場合、本発明の効果、すなわち、製造段階での塗布面の点状欠陥の発生を抑制する観点から好ましい。

【0037】記録層を形成する塗布液を支持体上に塗布した後、乾燥する過程では、通常は塗布体を高温状態にある領域を通過させながら必要に応じて塗布表面に風を吹き付けることにより行われるが、この場合、塗布表面温度は水分の蒸発熱のために雰囲気温度より低くなるのが通常であり、乾燥のための熱エネルギーの供給は表面よりは支持体の裏面から記録層への熱伝達により主として行われる。

【0038】支持体がプラスチックフィルムから成る場合には、多孔質層がないために、支持体の裏面が接触する各種のローラー等の部分的な不均一さに起因する熱エネルギーの分布がそのまま塗布面に現れやすい為、不均一な乾燥を経由しやすくなり、その結果として点状の欠陥も生じやすい。

【0039】これに対して、支持体が多孔質層を有する 両面をポリオレフィン樹脂で被覆した紙支持体などの場 合には、熱のばらつきが紙層中で横方向に緩和され易い ためにこうした欠陥がより生じにくい。

【0040】本発明の記録用紙に用いられる支持体は、記録層側の表面特性が、JIS-B-0610に従って測定された断面曲線からカットオフ値0.8mmの条件で導かれる濾波うねり曲線について基準長さ2.5mmとして濾波最大うねりを測定したときに、最大うねりが4mm以下であることを特徴とする。

【0041】ここで、断面曲線は、記録紙の表面に直角な平面で切断した時、その切り口に現れる曲線であり、濾波うねり曲線とは上記の断面曲線から低域フィルターを用いて波長の短い表面粗さ成分を除去して得られる曲線である。またカットオフ値は濾波うねり曲線を求めるために減衰率-12dB/octの低域フィルターを用いたとき、その利得が70%になる周波数に対応する波長であり、最大うねりとは濾波最大うねり曲線の基準長さ内における最大波高(Wcu)を $\mu$ m単位で表したもの

である。

【0042】なお、本発明では、上記最大うねりは、任意の10カ所についてその最大うねりを測定し、その平均値として求めた値を使用する。

【0043】本発明においては、上記表面うねりは、触針式表面粗さ計(サーフコム1500A、東京精密株式会社製)を使用して行った。

【0044】上記において、支持体の平滑度を濾波最大 うねりで表すことは、支持体の平滑性を表す方法が、本 発明の効果を得るのに必要である支持体表面の、より短 い波長の凹凸によってはあまり影響を受けにくいためで ある。

【0045】空隙を有する記録層の乾燥膜厚が厚いほど、より波長の長い凹凸の方が点状欠陥に対する影響がより大きくなる。特に乾燥膜厚が30μmを超えると支持体表面の微小な凹凸の寄与は殆どなくなり、より波長の長いうねりの寄与が一般には顕著になる。

【0046】乾燥膜厚の下限は被膜の空隙率や要求される空隙量により決まるが、一般には $15 \mu$  m以上、好ましくは $20 \mu$  m以上である。

【0047】支持体の表面の上記Wcu が $4\mu$ mを超えると空隙層の塗布乾燥時に点状の故障が生じやすくなる。好ましくはWcu が $3\mu$ m以下であり、特に好ましくは $2\mu$ m以下である。

【0048】本発明の構成に近い技術として、前記特開平8-174992号公報には、鏡面光沢度が80%以上のポリオレフィン被覆紙支持体上に、平均粒径が10nm以下の無機微粒子と親水性バインダーを使用し、高い光沢度を得るインクジェット記録用紙が記載されているが、高い光沢度として要求される平面特性は、本発明の如き比較的波長の長い凹凸ではなく、波長の短い凹凸であり本願とは明確に異なるものである。

【0049】また、光沢度に及ぼす支持体の平面性の影響は、記録層の乾燥膜厚は大きくなるほど支持体の平面性の影響を受けにくくなり専ら空隙層自体の光沢性に依存してくるようになるが、本発明の効果である点状故障は乾燥膜厚の増大に伴い一般に増加し、乾燥膜厚が増加するほど支持体の影響が出やすいという特徴がある。

【0050】前記の波長の短い微小な凹凸は上記のごとき測定機で、高域カットオフを行わないで条件で測定することにより求められる(例えばJIS-B-0601に記載された方法)が、この場合波長の短い凹凸も全て測定される。

【0051】本発明の効果は上記うねりの条件が本発明の範囲内に入っていれば得ることが出来るが、上記波長の短い成分を入れて測定した場合 JIS-B-0601 に従って求められる基準長さ2. 5 mm当たりの最大高さが 6  $\mu$  m以下であるのが好ましく、特に 4  $\mu$  m以下が最も好ましい。

【0052】次に、特に好ましく用いられるポリオレフ

ィンで両面を被覆した紙支持体について説明する。

【0053】紙支持体に用いられる原紙は木材パルプを 主原料とし、必要に応じて木材パルプに加えてポリプロ ピレンなどの合成パルプあるいはナイロンやポリエステ ルなどの合成繊維を用いて抄紙される。木材パルプとし てはLBKP、LBSP、NBKP、NBSP、LD P、NDP、LUKP、NUKPのいずれも用いること が出来るが短繊維分の多いLBKP、NBSP、LBS P、NDP、LDPをより多く用いることが好ましい。 但し、LBSPおよびまたはLDPの比率は10重量% 以上、70重量%以下が好ましい。

【0054】上記パルプは不純物の少ない化学パルプ (硫酸塩パルプや亜硫酸塩パルプ)が好ましく用いら れ、又、漂白処理を行って白色度を向上させたパルプも 有用である。

【0055】原紙中には、高級脂肪酸、アルキルケテンダイマー等のサイズ剤、炭酸カルシウム、タルク、酸化チタンなどの白色顔料、スターチ、ポリアクリルアミド、ポリビニルアルコール等の紙力増強剤、蛍光増白剤、ポリエチレングリコール類等の水分保持剤、分散剤、4級アンモニウム等の柔軟化剤などを適宜添加することが出来る。

【0056】抄紙に使用するパルプの濾水度はCSFの規定で $200\sim500cc$ が好ましく、また、叩解後の繊維長がJIS-P-8207に規定される24メッシュ残分重量%と42メッシュ残分の重量%との和が30乃至70%が好ましい。なお、4メッシュ残分の重量%は20重量%以下であることが好ましい。

【0057】原紙の坪量は60乃至250gが好ましく、特に90万至200gが好ましい。原紙の厚さは50万至250μmが好ましい。

【0058】原紙は抄紙段階または抄紙後にカレンダー処理して高平滑性を与えることも出来る。原紙密度は0.7乃至1.2  $g/m^2$  (JIS-P-8118)が一般的である。更に原紙剛度はJIS-P-8143に規定される条件で20乃至200gが好ましい。

【0059】原紙表面には表面サイズ剤を塗布しても良く、表面サイズ剤としては前記原紙中に添加できるサイズ剤と同様のサイズ剤を使用できる。

【0060】原紙のpHはJIS-P-8113で規定された熱水抽出法ににより測定された場合、5~9であることが好ましい原紙表面および裏面を被覆するポリオレフィンとしてはポリエチレンが特に好ましく、主として低密度のポリエチレン(LDPE)および/または高密度のポリエチレン(HDPE)であるが他のLLDPE(線状低密度ポリエチレン)やポリプロピレン等も一部使用することが出来る。

【0061】特にインク受容層側のポリエチレン層は写 真用印画紙で広く行われているようにルチルまたはアナ ターゼ型の酸化チタンをポリエチレン中に添加し、不透 9

明度および白色度を改良したものが好ましい。酸化チタン含有量はポリエチレンに対して概ね3~20重量%、好ましくは5~15重量%である。

【0062】原紙の表裏のポリエチレンの使用量はインク受容層やバック層を設けた後で低湿および高湿化でのカールを最適化するように選択されるが、概ねインク受容層側のポリエチレン層が20~50  $\mu$  m、バック層側が10~40  $\mu$  mの範囲である。

【0063】更に上記ポリエチレン被覆紙支持体は以下の特性を有していることが好ましい。

【0064】①引っ張り強さ: JIS-P-8113で 規定される強度で縦方向が2乃至30kg、横方向が1 乃至20kgであることが好ましい。

【0065】②引き裂き強度はJIS-P-8116による規定方法で縦方向が10万至300g, 横方向が2

0乃至400gが好ましい。

【0066】③クラーク剛度:20~400g/100が好ましい。

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【0067】④圧縮弾性率≥10<sup>3</sup>kgf/cm<sup>2</sup> ⑤表面平滑度: JIS-P-8119に規定されるベック平滑度が500秒以上、特に1000秒以上が好ましい。

【0068】⑥表面光沢度: JISZ-8741に規定された方法で75度の角度で測定した時、30%以上、好ましくは70%以上、特に好ましくは90%以上。

【0069】⑦表面白色度: JIS-Z-8722に記載された方法で測定し、JIS-Z-8729に従って表示したとき、

[0070]

【外1】

L\*は85%以上、特に90%以上が好ましい。また、(a\*, b\*) は

(-2, 2)、(4, 2)、(4, -8) および(-3, -8) で囲ま

#### れる範囲の色鯛が好ましい。

【0071】⑧不透明度: JIS-P-8138に規定 20 された方法で測定したときに50%以上、特に90%以上、最も好ましくは94%以上が好ましい。

【0072】上記支持体と記録層の接着強度を大きくする等の目的で、記録層の塗布に先立って、支持体にコロナ放電処理や下引処理等を行うことが好ましい。

【0073】本発明においては、支持体上に親水性バインダーと無機微粒子を含有する空隙層を記録層として少なくとも1層有する。

【0074】上記無機微粒子としては、低屈折率で粒径の小さな無機微粒子が好ましく、例えば、シリカ、コロイダルシリカ、珪酸カルシウム、炭酸カルシウム、ベーマイト水酸化アルミニウムまたはその水和物等が上げられるが、好ましくはシリカである。

【0075】シリカ微粒子は製造法により乾式法と湿式法に大別され、乾式法微粒子シリカとしてはハロゲン化珪素の高温での気相法加水分解による方法、およびケイ砂とコークスを電気炉でアーク法により加熱還元気化しこれを空気酸化する方法が知られている。また、湿式法シリカとしては珪酸塩の酸分解により活性シリカを生成した後、適度に重合させて凝集・沈殿させて得られる。

【0076】本発明においてはシリカ微粉末の中でも、 特に気相法により合成された無水シリカが特に空隙率と 強い皮膜強度が得られる点で好ましい。

【0077】上記無機微粒子の平均粒径は、その1次粒子として $0.1\mu$ m以下のものが好ましい。

【0078】無機微粒子が気相法シリカである場合には 1次粒子の平均粒径が $0.003\sim0.03\mu$ mであ 9. 特に $0.006\sim0.02\mu$ mが最も好ましい。気 相法シリカは塗布液中で2次凝集してより大きな粒子を 形成することができるが、この場合、2次凝集粒子の平

均粒径は0.03~0.2μmが好ましい。

【0079】上記において無機微粒子の平均粒径は、粒子そのものあるいは空隙層の断面や表面を電子顕微鏡で観察し、100個の任意の粒子の粒径を求めてその単純平均値(個数平均)として求められる。ここで個々の粒径はその投影面積に等しい円を仮定したときのその直径で表したものである。

【0080】本発明の記録用紙において、上記無機微粒子と組み合わせて用いられる親水性バインダーとしては、ポリビニルアルコールおよびその誘導体、ポリアルキレンオキサイド、ポリビニルピロリドン、ポリアクリルアミド、ゼラチン、ヒドロキシルエチルセルロース、カルボキシルメチルセルロース、プルラン、カゼイン、デキストラン等を用いることができるが、インクが含有する高沸点有機溶媒や水に対する膨潤性や溶解性が低い親水性バインダーを使用するのが印字直後の皮膜強度の点から好ましい。

【0081】本発明では特にポリビニルアルコールまたはその誘導体が好ましく、中でも平均重合度が1000以上、最も好ましくは平均重合度が2000以上のポリビニルアルコールまたはその誘導体である。また、ケン化度は70~100%が好ましく、特に80~100%が最も好ましい。

【0082】上記親水性バインダーは2種以上併用することもできるが、この場合であってもポリビニルアルコールまたはその誘導体を少なくとも50重量%以上含有してるのが好ましい。

【0083】上記ポリビルアルコール誘導体としては、カチオン変性ポリビニルアルコール、アニオン変性ポリビニルアルコールまたはノニオン変性ポリビニルアルコールが上げられる。

【0084】カチオン変性ポリビニルアルコールは、カチオン性基を有するエチレン性不飽和単量体と酢酸ビニルとの共重合体をケン化することにより得られる。

【0085】カチオン性基を有するエチレン性不飽和単 量体としては、例えばトリメチルー(2ーアクリルアミ ドー2,2ージメチルエチル)アンモニウムクロライ ド、トリメチルー(3ーアクリルアミドー3,3ージメ チルプロピル)アンモニウムクロライド、Nービニルイ ミダゾール、Nービニルー2ーメチルイミダゾール、N ー(3ージメチルアミノプロピル)メタクリルアミド、 ヒドロキシルエチルトリメチルアンモニウムクロライ ド、トリメチルー(ーメタクリルアミドプロピル)アン モニウムクロライド、Nー(1,1ージメチルー3ージ メチルアミノプロピル)アクリルアミド等が挙げられ る。

【0086】カチオン変性ポリビニルアルコールのカチオン変性基含有単量体の比率は、酢酸ビニルに対して0.1~10モル%、好ましくは0.2~5モル%である。

【0087】カチオン変性ポリビニルアルコールの重合 度は通常500~4000、好ましくは1000~40 00が好ましい。

【0088】また、酢酸ビニル基のケン化度は通常60 ~100モル%、好ましくは70~99モル%である。

【0089】アニオン変性ポリビニルアルコールは例えば、特開平1-206088号公報に記載されているようなアニオン性基を有するポリビニルアルコール、特開昭61-237681号、および同63-307979号公報に記載されているような、ビニルアルコールと水溶性基を有するビニル化合物との共重合体、及び特開平7-285265号公報に記載されているような水溶性基を有する変性ポリビニルアルコールが挙げられる。

【0090】また、ノニオン変性ポリビニルアルコールとしては、例えば、特開平7-9758号公報に記載されているようなポリアルキレンオキサイド基をビニルアルコールの一部に付加したポリビニルアルコール誘導体、特開平8-25795号公報に記載された疎水性基を有するビニル化合物とビニルアルコールとのブロック共重合体等が挙げられる。

【0091】本発明の記録用紙の空隙層の親水性バインダーに対する無機微粒子の比率は重量比で5倍以上であることが、高い空隙率と高い皮膜強度を得る上で必要である。5倍未満である場合には、空隙率が低下して十分なインク吸収容量が得られにくくなり、また、インクジェット記録後に、親水性バインダー中に残存する高沸点有機溶媒により皮膜の強度が低下しやすい。好ましい無機微粒子の親水性バインダーに対する比率は6以上である。

【0092】親水性バインダーに対する無機微粒子の比率の上限は、皮膜のひび割れ性能から概ね20以下であ

る。

【0093】本発明の記録用紙の空隙層中には前記親水性バインダーと架橋し得る硬膜剤を添加するのが空隙層の造膜性の改良、皮膜の耐水性、および本発明の目的である印字後の皮膜強度を改善する点で好ましい。そのような硬膜剤としてはエポキシ基、エチレンイミノ基、活性ビニル基等を含有する有機硬膜剤、クロムみょうばん、ほう酸、あるいはほう砂等の無機硬膜剤が挙げられる。

【0094】親水性バインダーがポリビニルアルコールである場合には特に、分子中に少なくとも2個のエポキシ基を有するエポキシ系硬膜剤、ほう酸またはその塩、ほう砂が好ましい。ほう酸としてはオルトほう酸だけでなく、メタほう酸や次ほう酸等も使用出来る。

【0095】上記硬膜剤の添加量は上記親水性バインダ -1g当たり1~200mg、好ましくは2~100m gである。

【0096】本発明のインクジェット記録用紙のインク 受容性層側の任意の層中には、必要に応じて各種の添加 剤を含有させることが出来る。

【0097】例えば、特開昭57-74193号公報、同57-87988号公報及び同62-261476号公報に記載の紫外線吸収剤、特開昭57-74192号、同57-87989号公報、同60-72785号公報、同61-146591号公報、特開平1-95091号公報及び同3-13376号公報等に記載されている退色防止剤、アニオン、カチオンまたはノニオンの各種界面活性剤、特開昭59-42993号公報、同59-52689号公報、同62-280069号公報、同61-242871号公報および特開平4-219266号公報等に記載されている蛍光増白剤、硫酸、リン酸、酢酸、クエン酸、水酸化ナトリウム、水酸化カリウム、炭酸カリウム等のpH調整剤、消泡剤、ジエチレングリコール等の潤滑剤、防腐剤、増粘剤、帯電防止剤、マット剤等の公知の各種添加剤を含有させることもできる。

【0098】本発明の記録用紙のインク吸収性側の任意の構成層中には、画像の耐水化剤として特開昭56-84992号公報のポリカチオン高分子電解質、特開昭57-36692号公報の塩基性ラテックスポリマー、特公平4-15744号公報、特開昭61-58788号公報、同62-174184号公報等記載のポリアリルアミン、特開昭61-47290号公報記載のアルカリ金属弱酸塩等を一種以上用いることができる。

【0099】本発明のインクジェット記録用紙におけるインク記録面側の塗布固形分の量は概ね $5\sim40g/m^2$ が好ましく、 $10\sim30g/m^2$ がより好ましい。

【0100】本発明の記録用紙をインクジェット用記録 用紙として使用する場合には、空隙容量として記録用紙  $1\,\mathrm{m}^2$ 当たり $10\sim40\,\mathrm{m}$  l、好ましくは $15\sim30\,\mathrm{m}$  1になる範囲に調整されることが好ましい。

【0101】但し、空隙容量は J. TAPPI 紙パルプ試験方法 No. 51-87紙及び板紙の液体吸収性試験方法 (プリストー法) に記載された方法で記録用紙のインク吸収性側を測定した時、吸収時間が 2秒における液体転移量  $(m1/m^2)$  で表される。なお、この時使用する液体は純水(イオン交換水)であるが、測定面積の判別を容易にするために 2 %未満の水溶性染料を含有していても良い。

【0102】本発明の記録用紙は、前記した空隙層を有する記録層を2層以上有していても良く、この場合、2層以上の空隙層の無機微粒子の親水性バインダーに対する比率はお互いに異なっていてもよい。

【0103】また、上記空隙層以外に、空隙層を有さず、インクに対して膨潤性の層を有していても良い。

【0104】このような膨潤層は空隙層の下層(支持体に近い側)あるいは空隙層の上層(支持体から離れた側)に設けても良く、更には空隙層が2層以上有る場合には空隙層の間に設けられても良い。かかる膨潤性層には通常親水性バインダーが用いられ、ここに用いられる親水性バインダーの例としては、前記空隙層に用いられる親水性バインダーが挙げられる。

【0105】本発明の記録用紙のインク吸収性層を有する側とは反対側にはカール防止や印字直後に重ね合わせた際のくっつきやインク転写を更に向上させるために種々の種類のバック層を設けることが好ましい。

【0106】バック層の構成は支持体の種類や厚み、インク吸収性層の構成や厚みによっても変わるが一般には親水性バインダーや疎水性バインダーが用いられる。バック層の厚みは通常は $0.1\sim10\mu$ mの範囲である。【0107】また、バック層には他の記録用紙とのくっつき防止、筆記性改良、さらにはインクジェット記録装置内での搬送性改良のために表面を粗面化できる。この目的で好ましく用いられるのは粒径が $2\sim20\mu$ mの有機または無機の微粒子である。

【0108】次に本発明の記録用紙を製造する方法について説明する。

【0109】本発明の記録用紙は、支持体上に少なくとも空隙層を有する記録層を塗布乾燥して得られる。空隙層を形成する塗布液(親水性バインダー、無機微粒子および必要に応じて適宜添加される前記添加剤を含有する)を支持体上に塗布し、乾燥されるが、この際、塗布液の温度は通常は30~50℃の範囲のものが用いられ、支持体上に塗布後にいったん冷却させてから乾燥させると乾燥時の点状故障が軽減される。

【0110】 塗布液をいったん冷却する事により、塗布液の粘度が著しく増大し、塗膜の流動性が低下して搬送時の振動や風の影響による塗膜のムラが大幅に減少する。 塗膜のムラが有る場合には、膜厚が増大した箇所での点状故障が増大するだけでなく、部分的に空隙容量に

【0111】塗膜の温度は塗布液の温度より10℃以上、好ましくは20℃以上低下させてその状態で水分や低沸点有機溶媒を一部蒸発させる。この状態に達すると 塗膜の粘度はいっそう急速に増大しゲル化状態に近づく

ムラが生じて画像品質に重大な影響を起こしかねない。

**塗膜の粘度はいっそう急速に増大しゲル化状態に近づくために、これを過ぎると乾燥温度を増加させても塗膜が動かなくなり高温の風を送り急速に乾燥してもムラや点状故障のない良好な塗膜面が得られる。** 

【0112】いったん冷却する温度は塗布液の無機微粒子の粒径、濃度、親水性バインダーの種類や濃度、硬膜剤の種類や量、更には無機微粒子と親水性バインダーとの相互作用など種々の因子により変わりうるが、通常は0~20℃、好ましくは5~15℃である。

【0113】冷却時間は冷却温度や湿潤膜厚などにより変わりうるが通常は5~200秒、好ましくは10~60秒である。

【0114】冷却後の乾燥は、通常は徐々に乾燥温度を 挙げるのが好ましい。通常は室温付近の温度で一定時間 乾燥後、最終的には40~60℃の温風で乾燥される。

【0115】上記の目的のために、塗布液の粘度特性は特に重要である。好ましくは塗布温度で5~500cp程度の塗布液であり、冷却時に1000cp以上、特に好ましくはゲル化状態に成るように調整される。

【0116】特に塗布液温度と冷却時の温度の粘度比が 100倍以上になるようにするのが好ましい。

【0117】上記空隙層を支持体上に塗布する方法は公知の方法から適宜選択して行うことが出来る。塗布方式としては、ロールコーティング法、ロッドバーコーティング法、エアナイフコーティング法、スプレーコーティング法、カーテン塗布方法あるいは米国特許第2,681,294号公報記載のホッパーを使用するエクストルージョンコート法が好ましく用いられる。

【0118】次に本発明の記録用紙をインクジェット記録用紙として使用する場合の水性インクについて以下に説明する。

【0119】水性インクは、通常は水溶性染料及び液媒体、その他の添加剤から成る記録液体である。水溶性染料としてはインクジェットで公知の直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が使用できるが直接染料、または酸性染料が好ましい。

【0120】水性インクの溶媒は水を主体としてなるが、インク液が乾燥した際に染料が析出してノズル先端やインク供給経路での目詰まりを防止するために、通常沸点が約120℃以上で室温で液状の高沸点有機溶媒が使用される。高沸点有機溶媒は水が蒸発した際に染料などの固形成分が析出して粗大析出物の発生を防止する作用を持つために水よりはるかに低い蒸気圧を有することが要求される一方、水に対して混和性が高い必要があ

【0121】そのような目的で高沸点有機溶媒としては高沸点の有機溶媒が通常多く使用されるが、具体例としては、エチレングリコール、プロピレングリコール、ジェチレングリコール、トリエチレングリコール、ジェチレングリコールモノブチルエーテル、トリエチレングリコールモノブチルエーテル、トリエチレングリコールモノブチルエーテル、グリセリンモノメチルエーテル、1,2,3ープタントリオール、1,2,4ープタントリオール、1,2,4ープタントリオール、1,2,4ーペンタントリオール、トリエタノールアミン、ポリエチレングリコール(平均分子量が約300以下)等のアルコール類が挙げられる。また、上記した以外にも、ジメチルホルムアミド、Nーメチルピロリドン等も使用できる。

【0122】これらの多くの高沸点有機溶媒の中でも、ジエチレングリコール、トリエタノールアミンやグリセリン、トリエタノールアミン等の多価アルコール類、トリエチレングリコールモノブチルエーテルの多価アルコールの低級アルキルエーテル等は好ましいものである。【0123】水性インクが含有するその他の添加剤としては、例えばpH調節剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、湿潤剤、界面活性剤、及び防

【0124】水性インク液は記録用紙に対する濡れ性を 良好にするため及びインクジェットノズルからの吐出を 安定化させる目的で、25℃において、25~50dy ne/cm、好ましくは28~40dyne/cmの範 囲内の表面張力を有するのが好ましい。

錆剤、等が挙げられる。

【0125】また、水性インクの粘度は通常25℃において $2\sim8$  c p、好ましくは $2.5\sim5$  c pである。

【0126】 水性インクの p H は通常 4~10の範囲である。

【0127】インクノズルから吐出される最小インク液滴としては $1\sim3$ 0×10 $^3$ nlの容量の場合、記録紙上で約20 $\sim6$ 0 $\mu$ mの直径の最小ドット径が得られるので好ましい。このようなドット径で印字されたカラープリントは高画質画像を与える。好ましくは $2\sim2$ 0× $10^{-3}$ nlの容積を有する液滴が最小液滴として吐出される場合である。

【0128】また、前記水性インクが、少なくともマゼンタおよびシアンについて、各々濃度が2倍以上異なる2種類のインクで記録する方式において、ハイライト部では低濃度のインクが使用されるためにドットの識別がしにくくなるが、本発明はかかる記録方式を採用した場合も適用できる。

【0129】インクジェット記録方法において、記録方法としては、従来公知の各種の方式を用いることができ、その詳細はたとえば、インクジェット記録技術の動向(中村孝一編、平成7年3月31日、日本科学情報株式会社発行)に記載されている。

【0130】本発明のインクジェット記録方法において、最大インク量における高沸点有機溶媒量に対する空隙容量を3倍以上にする方法は高沸点有機溶媒のインク中の比率を下げる、最大吐出インク量を出来るだけ少なくする、記録用紙の空隙容量を膜厚を出来るだけ多くする等の方法を適宜組み合わせて最適な条件を設定し選択される。

【0131】以上、本発明の記録用紙をインクジェット 用の記録用紙として説明してきたが、本発明の記録用紙 は、インクジェット記録以外にも、感熱転写方式(熱溶 融性のインクを含有する記録材料をインクシート支持体 側から加熱して溶融させて記録させるいわゆる溶融型熱 転写方式、および昇華型染料と高軟化性樹脂からなる記 録材料溶融型熱転写方式と同様にして加熱して記録する いわゆる昇華型熱転写方式)用の記録用紙および電子写 真方式等の記録用紙にも適用できる。

#### [0132]

【実施例】以下に本発明の実施例を挙げて説明するが、 本発明はこれらの例に限定されるものではない。

#### 【0133】実施例1

 $160 \, \mathrm{g/m^2}$ の写真用原紙の両面をポリエチレンで被覆した紙支持体(記録面側の厚さ  $40 \, \mu \, \mathrm{m}$ のポリエチレン層中にアナターゼ型二酸化チタンを  $13 \, \mathrm{m} \, \mathrm{m}$ 含有。 裏面側のポリエチレン層の厚みは  $25 \, \mu \, \mathrm{m} \, \mathrm{cr}$ ポリエチレン層の上に  $15 \, \mathrm{m} \, \mathrm{m}$  に  $15 \, \mathrm{m}$  でポリエチレン層の上に  $15 \, \mathrm{m}$  に  $15 \, \mathrm{m}$  に 15

【0134】上記ポリエチレン被覆紙の特性として、光沢度、Wcu、最大高さ(JIS-0601に従って求められる基準長さが2.5mm当たりの最大高さ、 $\mu m$ 単位)を求め、表1に示した。

【0135】次に平均粒径が約7nmの1次微粒子シリカ粉末150gを純水1000ml中に添加し、高速ホモジナイザーで分散して青白い澄明な分散液を得た。次にこのシリカ水分散液(I)中に、平均重合度が3500でケン化度が88%の2%ポリビニルアルコール水溶液(II)(酢酸エチルを6重量%含有)1000mlを徐々に添加した。ついで硬膜剤として4%ほう砂水溶液40mlを添加し、高速ホモジナイザーにて分散して白色半透明状の塗布液を得た。この液はシリカをポリビニルアルコールに対して重量比で7.5倍含有している。また、上記塗布液の粘度はB型粘度計で測定したときに、40℃で60cp、15℃で測定したとき5万cpであった。

【0136】ついで上記のようにして得られた40℃の 塗布液を、上記のポリエチレン被覆紙の記録面側に塗布 し、塗布皮膜温度が15℃以下に成るようにいったん冷 却させた(20 秒間)。ついで20 ℃の風を30 秒間、 25 ℃の風を30 秒間、35 ℃の風を60 秒間、更に4 5℃の風を120秒間順次吹き付けて乾燥し、さらに25℃、相対湿度50%の雰囲気を30秒間通過させて調湿して記録用紙-1を作製した。

【0137】次に、記録用紙-1において、支持体の原紙として平滑性の異なる種々の原紙を使用し記録用紙-1と同じポリエチレン層を表裏に被覆した記録用紙-2~4を記録用紙-1と同様にして作製した。記録用紙-1~4のポリエチレン被覆後の光学的特性および平滑性を表1に示した。

【0138】記録用紙-1~4は塗布乾燥後、ロール状 10 に巻いた状態で39℃で3日間保存した。

【0139】得られた記録用紙について以下の項目について評価した。

【0140】(1)空隙容量

熊谷理機工業株式会社製、Bristow試験機II型 (加圧式)を使用し、接触時間2秒間における転移量 (ml/m²)を空隙容量として求めた。

【0141】(2)インク吸収性

空隙容量を測定したのと同じ試験機を用い、接触時間が0.5秒における転移量 $(m1/m^2)$ からインク吸収性を求めた。

【0142】(3)光沢度

日本電色工業株式会社製変角光度計 (VGS-101DP)で75度鏡面光沢を測定した。

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【0143】(4)故障欠陥

10×10cmの塗布試料について、表面の点状欠陥個数を調べた。

【0144】(5)皮膜強度

セイコーエプソン株式会社製インクジェットプリンター、MJ-5100Cでベタ印字後、23℃、相対湿度が80%で24時間保存してから同じ環境で引っ掻き強度試験機(ヘイドン・トライボギア、新東科学株式会社製)を用い、先端が0.3mmφのサファイヤ針に、0~100gの連続荷重をかけて皮膜強度を試験し、皮膜が破壊される強度を皮膜強度とした。

【0145】この評価方法で概ね30g以上であれば実 用上十分高い皮膜強度を有していると言える。

【0146】なお、(1)(2)において、使用したインクはジエチレングリコールを20重量%、水溶性マゼンタ染料を1重量%含有するインクを使用した。結果を表1に示す。

[0147]

【表1】

記録用紙一	支持体の特性			記録層無機敵粒子/	記録用紙の特性					
	光沢度	Wcm	最大高さ	親水性ベゾー	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度
記録用紙-1 (本発明) 記録用紙-2 (本発明) 記録用紙-3 (本発明) 記録用紙-4 (比較例)	94% 93% 91% 90%	1.2 µm 2.3 µm 3.5 µm 5.2 µm	1.9µm 4.1µm 5.2µm 6.3µm	7.5 7.5 7.5 7.5	38 µm 38 µm 38 µm 38 µm	24ml 24ml 24ml 24ml	16m1 16m1 16m1 16m1	61% 61% 61% 53%	0 1 12 >100	72 g 69 g 70 g 73 g

【0148】表1の結果から、原紙の種類を変えてポリエチレン樹脂で被覆後の表面特性を変化させた場合、W cu が $4\mu$  m以下である記録用紙 $-1\sim3$  は、Wcu が $4\mu$  mを超える記録用紙-4に比べて故障欠陥が少ないことがわかる。

【0149】特にWa が 2 μ m以下である支持体を使用 40 した場合には故障欠陥が 0 で好ましい。

【0150】また、支持体の差により、空隙容量や、インク吸収性は殆ど影響を受けず、乾燥膜厚が $30\mu$  m以上で、高い空隙率(大凡63%)を有しているために通常のインクジェット記録でほぼ十分な空隙容量を保持している。

#### 【0151】実施例2

実施例1で作製した記録用紙-1において、記録面側のポリエチレン層の厚みを表2に示すように変化させたポリエチレン被覆紙支持体を用意し実施例1で作製した空 50

隙層を形成する塗布液を実施例1と同様に塗布して記録用紙-21~24を作製した。一方、実施例1で作製した記録用紙-1において、表側のポリエチレン層を原紙上に塗設直後に表面を種々の片づけ処理を行い、表面特性の異なる記録用紙-25~27を記録用紙-1と同様にして作製した。

【0152】記録用紙-25の支持体はいわゆる絹目面と称されるようなピッチの長さが数百 $\mu$ m単位の片付けであり、記録用紙-27の支持体は片づけはいわゆるマット面と称されるような微細な無光沢面である。記録用紙-26はこれらの中間である。

【0153】更に、記録用紙-28の支持体は記録用紙-1の支持体表面を40℃のアセトン溶液で処理して粗面化したものである。通常これらの粗面かは支持体と記録層の接着性の増大に効果がある。

【0154】記録用紙-21~28のポリエチレン被覆

紙の表面特性および記録層を塗布後の特性を実施例1と

[0155]

【表2】

同様にして評価した。結果を表2に示す。

記録用紙	ポリエチレン層		支持体の特性			記錄層	記録用紙の特性		
	厚み (μm)	片付け	光沢度	Wcs	最大高さ	無機般粒子/ 親水性パインター	光沢度	故障欠陥	皮膜強度
記録用紙-21(本発明)	30 µ m	無	92%	1. 7 µ m	2.1 µ m	7.5	59%	0	71 g
紀録用紙-22(本発明)	20 µ m	無	85%	2.5 µ m	3.4 µ m	7.5	58%	2	70 g
記録用紙-23(本発明)	15 µ m	無	71%	3. 2 $\mu$ m	5. 2 µ m	7.5	58%	10	73 g
記録用紙-24(比較例)	10 µ m	無	56%	4. 7 µ m	7.1µm	7. 5	51%	90	68 g
記録用紙-25(比較例)	40 µ m	有	46%	5.8 µ m	7.8µm	7.5	50%	>100	44 9
記錄用紙-26(比較例)	40 µ m	有	9%	4.6µm	6.3 µ m	7.5	36%	>100	68 g
記録用紙-27(本発明)	40 $\mu$ m	有	5%	3.3 µ m	3. 2 $\mu$ m	7.5	41%	. 8	67 g
記録用紙-28(本発明)	40 µ m	粗面化	18%	2.3 µ m	3.1 µ m	7.5	53%	3	68 g

【0156】表20結果から、WCM が $4\mu$  m以下である 20本発明の記録用紙-21、22、および23は、比較の記録用紙-24に比較して故障欠陥が少ないことがわかる。また、実施例1と同様に特にWCM が $2\mu$  m以下の記録用紙-21が特に優れていることがわかる。

【0157】一方、ポリエチレン樹脂層の表面を片付け処理したり粗面化して支持体の光沢性が低いものを使用した場合であっても、Wcu が  $4~\mu$  m以下である記録用紙-27、28 は故障欠陥が少ないことがわかる。また片付け支持体の中でもWcu が  $4~\mu$  mを超える場合には故障

欠陥が急速に増加することがわかる。

#### 【0158】比較例1

実施例1で作製した記録用紙-4用のポリエチレン被覆紙支持体上に、実施例1で作製した塗布液を湿潤膜厚を変化させて表3に示すような乾燥膜厚を有する記録用紙-31~34を記録用紙-4と同様にして作製した。

【0159】実施例1と同様に評価して表3に示す結果を得た。

[0160]

【表3】

記録用紙	支持体の特性 記録 層 無機強粒子。		記録用紙の特性						
	Wcm	親水性バインダー	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥		
記録用紙-31(比較例) 記録用紙-32(比較例) 記録用紙-33(比較例) 記錄用紙-34(比較例)	5.2µm 5.2µm 5.2µm 5.2µm	7.5 7.5 7.5 7.5	45μm 30μm 25μm 20μm	29mi 19mi 16mi 12mi	21 ml 11ml 7ml 4ml	52% 51% 62% 64%	>100 >100 58 20		

【0161】表3の結果から、Wcu が $4\mu$ mを超える支持体を使用しても、乾燥膜厚を減少させていくと故障欠陥は低下してくるが、これに伴い空隙容量が徐々に低下してくるので、記録用紙 $-31\sim34$ は実用的に使用する事は出来ない。

【0162】実施例3

実施例1で作製した記録用紙-1~4において、微粒子

シリカを1次粒子の平均粒径が約20nmの気相法シリカに変えた以外は記録用紙-1~4と同様にして記録用紙-41~44を作製した。実施例1と同様に評価し、表4に示す結果を得た。

[0163]

【表4】

記録用紙	支持体の特性	記 録 唐 無機殺粒子/	記録用紙の特性						
		親水性パインダー	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度	
記録用紙-41(本発明)	1. 2 μ m	7. 5	38 µ m	26m1	19m1	54%	0	60 g	
記録用紙-42(本発明)	2.3 µ m	7. 5	38 µ m	26ml	19m1	52%	. 3	57 g	
記録用紙-43(本発明)	3.5 µ m	7. 5	38 µ m	26m1	19m/l	51%	15	58 g	
記錄用紙-44(比較例)	5. 2 $\mu$ m	7. 5	38 µ m	26m l	19m I	51%	>100	53 g	

【0164】表4の結果から、実施例1と同様の効果が得られることがわかる。但し、シリカの1次粒子の粒径の増大に伴い記録面の光沢性が実施例1より僅かに低下し、また、空隙容量は若干増加している。

### 【0165】比較例2

平均粒径が約7nmの1次微粒子シリカ粉末150gを 純水1000ml中に添加し、高速ホモジナイザーで分 散して青白い澄明な分散液を得た。次にこのシリカ水分 20 散液(I)中に、平均重合度が3500でケン化度が8 8%の2%ポリビニルアルコール水溶液(II) (酢酸エ チルを6重量%含有)2000mlを徐々に添加した。 ついで硬膜剤として4%ほう砂水溶液40mlを添加 し、高速ホモジナイザーにて分散して白色半透明状の塗 布液を得た。この液はシリカをポリビニルアルコールに 対して重量比で3.75倍含有している。

【0166】実施例1において使用した記録用紙 $-1\sim4$ のポリエチレンで被覆紙上に上記の塗布液を乾燥膜厚が実施例1と同じ様になるように湿潤膜厚が170 $\mu$ mになるように塗布し、実施例1に記載された方法で乾燥して記録用紙 $-51\sim54$ を作製した。実施例1と同様に評価し、表5に示す結果を得た。

【0167】 【表5】

記録用紙	支持体の特性	記録層 無機微粒子/	記録用紙の特性						
	Wcm	親水性パインダー	乾燥膜厚	空隙容量	インク吸収性	光沢度	故障欠陥	皮膜強度	
記録用紙-51(比較明) 記録用紙-52(比較明) 記録用紙-53(比較明) 記録用紙-54(比較例)	1. 2 µm 2. 3 µm 3. 5 µm 5. 2 µm	3. 75 3. 75 3. 75 3. 75	38 µ m 38 µ m 38 µ m 38 µ m	15m1 15m1 15m1 15m1	4m l 4m l 4m l 4m l	81% 80% 80% 78%	0 0 0 3	17g 15g 15g 14g	

【0168】表5に示す結果から、無機微粒子の親水性 バインダーに対する比率を5以下にした場合には、故障 欠陥は支持体としてWcu が4  $\mu$  mを超えるものを使用し てもほとんど生ぜず、記録面の光沢性も非常に高いが、 空隙容量が低下し、また、皮膜の強度が大きく低下する

ことがわかる。

[0169]

【発明の効果】以上、本発明に従えば、高インク吸収 40 性、高光沢性、高塗膜強度を有し、しかも点状故障を大きく減少させた記録用紙が得られる。

フロントページの続き

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